

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : H01L 51/20, H05B 33/04	A1	(11) International Publication Number: WO 00/26973
		(43) International Publication Date: 11 May 2000 (11.05.00)

(21) International Application Number: PCT/US99/25843  
(22) International Filing Date: 2 November 1999 (02.11.99)

(30) Priority Data:  
60/106,871 2 November 1998 (02.11.98) US  
09/419,870 18 October 1999 (18.10.99) US

(71) Applicant (for all designated States except US): DELTA V TECHNOLOGIES, INC. [US/US]; 7775 N. Casa Grande Highway, Tucson, AZ 85743 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): BRIGHT, Clark, I. [US/US]; 7850 N. Silverbell, No. 114-107, Tucson, AZ 85743 (US).

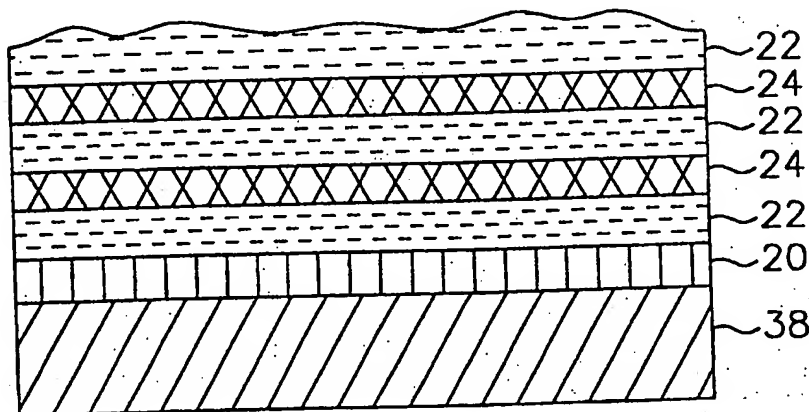
(74) Agent: AUCIELLO, Lucinda, G.; Christie, Parker & Hale, LLP, P.O. Box 7068, Pasadena, CA 91109-7068 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.  
With amended claims.

(54) Title: TRANSPARENT CONDUCTIVE OXIDES FOR PLASTIC FLAT PANEL DISPLAYS



## (57) Abstract

The present invention employs lightweight, flexible, plastic substrates for constructing flat panel displays, packaging materials and electro luminescence lamps. The display medium is protected from oxygen and moisture in order to avoid degradation. In the present invention, at least one layer with barrier and electrode characteristics is deposited over the substrate that has both a low enough resistivity to function as an electrode for the display and low oxygen and moisture permeability. For lower permeability and/or higher conductivity, multiple alternating layers of barrier materials and conductive materials are applied. The barrier material includes a thin metallic film, an organic polymer, a thin transparent dielectric, and a thin transparent conductive oxide. The conductive material includes a thin transparent conductive oxide, a thin transparent metallic film, and/or a metal nitride. Preferably there is a Polymer Multi Layer (PML) processed base coat deposited over the substrate. The base coat produces substrate smoothing, and more importantly, in combination with another layer, the base coat has vapor barrier properties. In the preferred embodiment, a PML processed top coat barrier layer is deposited before the coating contacts a surface, such as a roller. The PML processed top coat excludes moisture and atmospheric gases that chemically degrade the device performance.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakistan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## 1 TRANSPARENT CONDUCTIVE OXIDES FOR PLASTIC FLAT PANEL DISPLAYS

## FIELD OF THE INVENTION

5 This invention relates to composite substrates for flat panel displays (FPD), packaging materials and light sources (electro luminescence lamps) comprising a plastic substrate having thin film barrier and conductive layers, in particular, multiple thin alternating layers of metallic film, transparent conductive oxide (TCO), metal nitride, and organic polymers deposited over the plastic substrate.

## 10 BACKGROUND OF THE INVENTION

The use of portable electronic devices incorporating flat panel displays is prevalent and increasing rapidly. Because of the portable nature of these devices, it is desired to minimize both the size and weight and maximize durability. The display portion of the device is generally larger and denser as compared to the rest of the device, and is manufactured on glass  
15 substrates. Accordingly, a smaller, lighter and more durable portable electronic device is most effectively achieved with a smaller, lighter and shatterproof electronic device display.

Despite being lightweight, plastic has not been considered a viable substrate material to be used for the manufacture of flat panel displays for multiple reasons. Most importantly, flat panel displays with plastic substrates tend to fail prematurely due to degradation of the display  
20 medium and some metallic electrodes. In particular, the display medium and some metallic electrodes become degraded when atmospheric oxygen and water permeate the substrate and chemically degrade the active portion of the display matrix, which is generally comprised of liquid crystals and/or light emitting devices. Second, common optical quality plastic substrates, e.g. polyethylene terephthalate (PET), have limited thermal properties. In particular, there is  
25 a limited temperature range that allows useful optical quality (e.g. clarity, transparency, uniform index of refraction) to be maintained, while maintaining the requisite mechanical strength and properties of the substrate.

## SUMMARY OF THE INVENTION

30 The present invention is directed to the fabrication of flat panel displays on lightweight, flexible, plastic substrates. Because plastic substrates for FPDs are flexible, smaller and lighter than glass substrates, the electronic device with the plastic FPD is more portable, space-efficient and lightweight. In addition, electroluminescent and organic light emitting devices fabricated on flexible polymeric substrates in a coating process have lower manufacturing costs than those  
35 with glass substrates, and improved ruggedness.

A display medium of the flat panel display is sandwiched between two electrode layers. At least one of the electrodes is transparent for viewing of the display. The display medium is protected from oxidative degradation. In the present invention, at least one layer, having both

1 barrier characteristics and the ability to function as an electrode, is deposited over the substrate.  
In particular, the layer has both low oxygen and moisture permeability, and a low enough  
resistivity to function as an electrode for the display. For lower permeability and/or higher  
conductivity, multiple alternating layers of barrier materials and conductive materials are  
5 applied. In an alternative embodiment, the conductive layers are in direct contact. The barrier  
material includes at least one of an organic polymer, a transparent dielectric, a transparent metal  
nitride and/or a transparent conductive oxide. The conductive material includes at least one of  
a thin transparent conductive oxide, a thin transparent metallic film and/or a metal nitride.

10 Using a smoothing base coat layer over the plastic substrate imparts good optical quality  
throughout the substrate layers and provides a pristine surface for nucleation of the deposited  
conductive layer, e.g. TCO. The pristine surface smooths over any surface roughness of the  
plastic substrate, thereby adding to the FPD lifetime and optical quality. Additionally, a  
hardcoat layer is applied over the substrate in lieu of or in addition to the smoothing basecoat  
layer. The hardcoat layer provides increased barrier ability.

15 While the smoothing layer is applied by one of many well known non-vacuum liquid  
coating processes, e.g. preferably by Gravure, the base coat is fabricated through a polymer  
multilayer (PML) coating process. Related desirable coating processes are disclosed in U.S.  
Patents 5,547,508, 5,395,644, 5,260,095, U.S. Patent Application Number 08/939,594, filed  
September 29, 1997, entitled "*Plasma enhanced chemical deposition with low vapor pressure  
20 compounds*" herein incorporated by reference, *Thin Film Processes II*, chapters II-2, 4, 5, and  
IV-1, edited by John L. Vossen and Wermer Kern, Academic Press, 1991, ISBN 0-12-728251-  
3, *Deposition Technologies for Films and Coatings, Developments and Applications*, Rointan  
F. Bunshah et al, Noyes Publications, 1982, ISBN 0-8155-0906-5. Plasma PML processes  
(PML and liquid PML) are called liquid multilayer (LML) processes. The PML process for  
25 vacuum evaporation is used to deposit organic monomers over the plastic substrate. The  
organic monomer is then polymerized in-situ by electron beam or UV radiation. The PML  
process is compatible with physical vapor deposition processes for layers such as TCO layers.  
Both processes are carried out in combined sequences within a properly designed single vacuum  
chamber, however, multiple vacuum chambers are preferably used. The PML deposited organic  
30 polymer layer is used to produce substrate surface smoothing and improve barrier coatings in  
the multilayer structure. The benefit of a smooth substrate surface is that there is a clean surface  
for adhesion, nucleation, and growth of a deposited conductive layer, e.g. a TCO. Additionally,  
a PML deposited organic polymer layer provides protection of an underlying barrier layer in  
order to minimize holes or other defects in the layer so that there is low permeability.

35 A single layer coating with metal oxide layers, such as thin film dielectric coatings  
(alumina or silica or other certain metal oxides), or thick metallic film layers having optical  
densities greater than 2.0 on plastic flat panel displays does not render low enough permeability  
for the processing and manufacture of these displays with acceptable lifetimes. Even where

1 multiple layers of dielectrics, metals or the combination thereof are used, the improvement in  
performance is minimal. In order to provide barrier properties sufficient for optical quality  
plastic flat panel displays, a transparent dielectric barrier, such as  $\text{SiO}_{2-x}$  or  $\text{Al}_2\text{O}_{3-y}$ , is deposited  
over a plastic substrate. When dielectric layers are combined with PML deposited organic  
5 polymer layers, outstanding barrier properties are achieved on flexible plastic substrates.  
Alternatively to the dielectric layer, a barrier coating of ITO (called "indium tin oxide", which  
is actually "Tin doped indium oxide," a mixture of indium oxide and tin oxide) or another TCO  
barrier is deposited over the substrate. In yet another alternative embodiment, both TCO barrier  
layers and PML processed organic polymer layers are deposited over the plastic substrate.  
10 Moreover, in yet another alternative, both TCO barrier layers with PML processed organic  
polymer layers and the transparent dielectric barrier layers are deposited over the plastic or  
polymeric substrate. Multilayer structures of such organic and inorganic layers deposited over  
a plastic substrate exhibit significantly improved barrier properties as compared to inorganic,  
organic or metallic layers alone.

15 In an embodiment, a PML processed top coat polymer layer is applied before the  
previously deposited layer contacts a surface, such as a roller, thereby protecting the previously  
deposited layer. The PML processed top coat greatly enhances the exclusion of moisture and  
atmospheric gases that chemically degrade the display medium and decrease the device  
performance, even though the polymer topcoat is not, itself, a good barrier material.

20 Metal oxide dielectric barriers have previously been deposited by evaporation, sputtering,  
and chemical vapor deposition processes onto glass substrates. However, for achieving bulk  
material-like properties a high temperature deposition method is to be used which melts the  
plastic substrate, thereby negatively impacting the mechanical properties of the substrate. In  
the present invention, the PML process used for depositing an organic dielectric does not  
25 require such high temperatures and therefore does not significantly alter the mechanical  
properties of the substrate. However, organic polymer layers alone do not provide substantial  
barrier properties, particularly against water vapor.

When TCOs are deposited at low temperatures to accommodate the thermal and  
mechanical limits of the substrate, for example, by magnetron sputtering, electron-beam  
evaporation or plasma enhanced chemical vapor deposition (PECVD), the subsequent TCO  
30 coatings have less than bulk conductivity, i.e. low overall levels of conductivity. TCO films  
with a larger thickness deposited through these methods achieve acceptable conductive levels  
for portable electronic devices. However, these thick films of TCO are subject to cracking,  
crazing and, in some instances, delamination from the substrate, especially when they are  
processed by a heat treatment step or a coating process involving mechanical rollers (e.g. web  
35 coating). As a consequence, the TCO coating is deposited in a series of thin, separated layers,  
yet still maintain high conductive levels. Multiple thin layers of TCO avoid the problems

1 associated with thicker layers, and advantageously are electrically connected in parallel to provide adequate electrical performance characteristics.

5 The thin layers of TCO are preferably deposited in combination with the PML process, which leads to improved optical, electrical and mechanical performance. Superior surface properties (low surface roughness, and high optical quality), barrier properties (low vapor permeability) and mechanical properties result when TCO coatings are deposited by magnetron sputtering on a plastic substrate in combination with the PML process. Preferably, moderate annealing temperature conditions are used for TCO deposition. The resistivity of ITO ("Tin doped indium oxide"), a TCO, is a function of the oxygen and tin content, as well as the  
10 deposition conditions (e.g. temperature). Previously, low temperature depositions yielded high resistivity ITO layers, when a low resistivity for ITO was desired. The resistivity of ITO was shown to decrease with a thicker TCO layer. But as discussed previously, thick TCO layers are prone to cracking or crazing. Multiple thin layers of TCO, as described in the present invention, will not crack and will yield a lower resistivity. Moreover, the surface resistivity of a thin film  
15 of TCO in multiple layers is low for a given total film thickness, due to its improved microstructure.

In an embodiment, a polymer smoothing coating is deposited over the substrate. The smoothing coating is applied by a PML process or liquid coating. A TCO, metal nitride, or metal layer is then deposited over the smoothing layer. Additionally, multiple alternating layers  
20 of a protective polymer layer and an additional TCO, metal nitride, or metal layer is deposited. Preferably, the alternating layers are of the same material, e.g. TCO/polymer/TCO, etc.

In another embodiment, a polymer smoothing coating layer is optionally deposited over the substrate. Additionally, multiple alternating layers of polymer layers and metal oxide or metal nitride are deposited over the substrate. A TCO layer is then deposited over the top of  
25 multiple alternating layers. These multiple alternating layers together with the TCO have adequate barrier and conductivity characteristics.

In yet another embodiment, a substrate is coated with a TCO layer, a metal coating, and another TCO layer. This three layer configuration is called "optically enhanced metal," or an induced transmission filter and has similar characteristics as a single TCO layer. With the  
30 optically enhanced metal good conductivity, optical transmission and barrier properties are achieved. A similar structure of metal nitrides, e.g., silicon nitride, metal and another metal nitride layer functions equivalently.

In still another embodiment, a substrate is alternatively coated with an inorganic layer (such as TCO, metal nitride, or dielectric metal oxides), and polymer layers to provide both  
35 barrier and conductive properties.

## BRIEF DESCRIPTION OF THE DRAWINGS

The aspects of the present invention described above in summary and below in more detail as well as various advantageous aspects will become appreciated as the same becomes better understood with reference to the specification, claims and drawings wherein:

FIG. 1 is a cross-sectional view of a composite substrate for a flat panel display (FPD) of the present invention;

FIG. 2 is a cross-sectional view of an embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 3 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 4 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 5 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 6 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 7 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 8 is a schematic illustration of a coating apparatus for forming the conductive barrier layer of FIG. 1;

FIG. 9a is a schematic illustration of a laminating process for the FPD of FIG. 1;

FIG. 9b is a cross-sectional view of the FPD before undergoing a bonding process;

FIG. 9c is a cross-sectional view of the FPD after undergoing a bonding process;

FIG. 10 is a chart showing water permeability of an ITO film deposited on a polyethylene terephthalate (PET) substrate versus ITO film sheet resistance;

FIG. 11 is a chart showing water permeability of ITO film deposited on a PET substrate versus ITO film thickness;

FIG. 12 is a chart showing oxygen permeability of ITO film deposited on a PET substrate versus ITO film thickness;

FIG. 13 is a chart showing oxygen permeability of ITO film deposited on a PET substrate versus ITO film sheet resistance;

FIG. 14 is a chart showing transmittance and reflectance spectra (for an ITO layer over a silver film layer over an ITO layer over a PET substrate at a sheet resistance of 14 Ohms/Square) versus wavelength;

FIG. 15 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 29 Ohms/Square) versus wavelength;

FIG. 16 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 57 Ohms/Square) versus wavelength;

1 FIG. 17 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 65 Ohms/Square) versus wavelength;

FIG. 18 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 347 Ohms/Square) versus wavelength;

5 FIG. 19 is a cross-sectional view of an embodiment of a conductive barrier layer;

FIG. 20 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

FIG. 21 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

10 FIG. 22 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

FIG. 23 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

15 FIG. 24 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

FIG. 25 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

FIG. 26 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

20 FIG. 27 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

FIG. 28 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

25 FIG. 29 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

FIG. 30 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

FIG. 31 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1;

30 FIG. 32 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1; and

FIG. 33 is a cross-sectional view of an embodiment of conductive barrier layers of FIG. 1.

### 35 DETAILED DESCRIPTION OF THE INVENTION

A flat panel display (FPD) 1, of the present invention as shown in FIG. 1, employs lightweight, flexible, plastic substrates 38 for constructing FPDs. In between two plastic substrates of the flat panel display are at least two electrodes. At least one of the electrodes is



1 transparent for viewing of the display. A display medium 2 for the flat panel display is situated between the two electrodes. The display medium, as well as some electrode material, are protected from oxidative degradation and reaction or incorporation of moisture.

5 The displays are fabricated using plastic substrates such as various polyolefins, e.g. polypropylene (PP), various polyesters, e.g. polyethylene terephthalate (PET), and other polymers such as polyethylene naphthalate (PEN), polyethersulphone (PES), polycarbonate (PC), polyetherimide (PEI), polyarylate (PAR), polyimide (PI), and polymers with trade names ARTON® (Japanese Synthetic Rubber Co., Tokyo, Japan) and AVATREL™ (B.F. Goodrich, Brecksville, Ohio). See Appendix A for deposition temperature capabilities of the particular plastic substrate.

10 In the present invention, at least one layer, a conductive barrier layer 3 has both barrier characteristics (to protect the display medium and/or the metal electrode) and the ability to function as an electrode, and is deposited over the substrate to form a composite substrate, as shown in FIG. 19. In particular, layer 3 has both low oxygen and moisture permeability, and a low enough resistivity to function as an electrode for the display.

15 As shown in the general embodiments of FIGs. 2 through 7, conductive barrier layer 3 comprises at least one sublayer 3' deposited over the substrate, for instance a single ITO layer. In an embodiment, at least one pair of sublayers (a dyad of a polymer and a TCO, metal, or metal oxide) is deposited over the substrate. In an exemplary embodiment, multiple alternating sublayer pairs, comprised of the same materials as the original sublayer pair, are deposited over the substrate or over the previously deposited sublayer.

20 There are a myriad of possibilities for materials comprising the sublayers of the conductive barrier layer. FIGs. 2-7 illustrate generally only some of the more preferred embodiments of sublayer 3' materials for conductive barrier layer 3, while FIGs. 19-33 illustrate particularly the more preferred embodiments for the conductive barrier layer.

25 In an embodiment, a base coating 20 is deposited over the substrate 38. The base coating is a polymer smoothing coating applied by a PML process or an organic hardcoat deposited by a liquid coating process to render a hardcoated PET substrate that is abrasion resistant. A TCO 22 (or metal layer 12) is then deposited over the base coat, as shown in FIG. 3, and more particularly in FIG. 20. Additionally, multiple alternating layers of a protective polymer layer 24 and an additional TCO 22 (or metal layer 12) are additionally deposited, as represented by sublayer 3' in FIG. 3, and more particularly in FIGs. 21 and 22. Preferably, the alternating layers are of the same material, e.g. TCO/polymer/TCO, etc. FIG. 2 illustrates the embodiment of polymer/TCO/polymer without base coat 20. Alternatively, a metal conductor or reflector 12 overlays the top polymer layer 24 as in FIGs. 23-25, and 30.

35 In another embodiment shown in FIG. 26, a substrate is coated with a TCO layer, a metal coating, and another TCO layer. This three layer configuration is called an "optically enhanced metal," and has characteristics similar to a single TCO layer. With the optically enhanced

1 metal, good conductivity, transmission and barrier properties are achieved. Deposited on these  
three layers is preferably a polymer layer 24, that is alternating with the three layers.  
Alternatively, base coat 20 is deposited over the substrate as shown in FIG. 27. Additionally  
or alternatively, another dyad (a metal and TCO pair) is deposited over the top TCO layer, as  
5 shown in FIGs. 28 and 29. Additionally or alternatively as shown in FIG. 29, an additional  
polymer layer 24 (a polymer overcoat) is deposited over the previously deposited dyad. In  
another alternative, a thick metal layer 12 is deposited over the polymer overcoat layer, as also  
shown in FIG. 29. Alternatively, a metal nitride layer is substituted for one or more of the metal  
layers of these embodiments, for example, see FIGs. 31 and 32.

10 In still another embodiment, a substrate is alternatively coated with an inorganic layer  
(such as a TCO or dielectric metal oxides), and polymer layers to provide both barrier and  
conductive properties.

FIG. 33 illustrates a metal layer 12 sandwiched between two metal nitride layers 14.  
Alternatively, additional dyads (metal and metal nitride pair) are deposited over the metal  
15 nitride layer. Further embodiments of this dyad pair are similar to the TCO/ metal dyad pair  
embodiments of FIGs. 26-29, i.e. the TCO layers of FIGs. 26-29 are replaced by one or more  
metal nitride layers.

In an alternative embodiment, a dielectric layer replaces one or more TCO layers in the  
above described embodiments (see generally FIGs. 6 and 7). As shown in FIG. 7, multiple  
20 alternating layers of dielectric 17 and polymer layers 24 are deposited over the substrate 38.  
The number of multiple alternating layers (or dyads) vary, and is represented here by 3<sup>1</sup>,  
sublayers of the conductive barrier layer 3. A TCO layer 22 is then deposited over the top of  
multiple alternating layers. These multiple alternating layers together with the TCO have  
adequate barrier and conductivity characteristics as described in more detail below.

25 Each TCO layer 22 of the above embodiments is a single TCO layer. Alternatively, the  
TCO layer represents two TCO layers.

Preferably, metal layers that are alternating dyad pairs or in between TCO, metal nitride,  
or dielectric layers are thin. In addition, metal layers that are adjacent the display matrix, i.e.  
overlying the dyad layers, have a greater thickness than the sandwiched metal layers.

30 Sublayer 3<sup>1</sup> materials that provide barrier properties are thin transparent metal oxides 16,  
and/or thin transparent metallic films 12. The polymers 24 enhance barrier properties by  
reducing the number of holes and defects in the films upon which or under which, they are  
deposited. The metal oxide layers alternatively comprise dielectric layers 17 and/or transparent  
conductive oxide layers 22. The thickness for these barrier layers are in the nanometer and  
35 angstrom range. The thickness for the PML deposited layers are in the micron range. For  
example, improved barrier coating occurs when a PML deposited organic polymer layer (a base  
coat), and/or a metal oxide layer is placed over the plastic substrate. See Tables 2 and 3.

1 Sublayer 3<sup>1</sup> materials that provide conductive properties include a thin TCO 22, a thin  
transparent metallic film 12 (such as aluminum, silver, copper, gold, platinum, palladium, and  
alloys thereof), and a metal nitride 14 (such as transition metal nitrides, for example, titanium  
5 nitride, zirconium nitride, hafnium nitride, and nitrides of Group IVA, VA, and VIA elements  
of the Periodic Table, as well as nitrides of Group IIIB and IVB elements of the Periodic Table,  
for example: gallium nitride, silicon nitride, and aluminum nitride). The thickness for these  
conductive layers are in the nanometer and angstrom range. Preferably the TCO is formed by  
multiple thin layers deposited with electrical contact to each other, so that a low resistivity is  
10 achieved. Consequently, the TCO functions as both the electrode and a barrier.

10 In the preferred embodiment, there is a PML processed base coat 20 deposited over the  
substrate as shown in FIG. 3. The base coat produces substrate smoothing, and more  
importantly, in combination with other layers, the base coat has surprisingly effective vapor  
barrier enhancement properties because of the smoothing and protection characteristics. The  
sublayers are deposited in combination with the process illustrated in FIG. 8.

15 Using a smoothing base coat layer over the plastic substrate imparts good optical and  
barrier quality throughout the substrate layers and provides a pristine surface for nucleation of  
the deposited TCO electrode layer. The pristine surface smooths over any surface roughness  
of the plastic substrate, thereby adding to the FPD lifetime and optical quality.

In an exemplary embodiment, one or more metal oxide layers are replaced with a TCO.  
20 When TCO coatings, including ITO ("Tin doped indium oxide"), cadmium oxides ( $\text{CdSn}_2\text{O}_4$ ,  
 $\text{CdGa}_2\text{O}_4$ ,  $\text{CdIn}_2\text{O}_4$ ,  $\text{CdSb}_2\text{O}_6$ ,  $\text{CdGeO}_4$ ), tin oxides, indium oxides ( $\text{In}_2\text{O}_3$ ; Ga,  $\text{GaInO}_3$  (Sn, Ge),  
( $\text{GaIn}_2\text{O}_3$ ), zinc oxides ( $\text{ZnO(Al)}$ ,  $\text{ZnO(Ga)}$ ,  $\text{ZnSnO}_3$ ,  $\text{Zn}_2\text{SnO}_4$ ,  $\text{Zn}_2\text{In}_2\text{O}_5$ ,  $\text{Zn}_3\text{In}_2\text{O}_6$ ), and/or  
magnesium oxides ( $\text{MgIn}_2\text{O}_4$ ,  $\text{MgIn}_2\text{O}_4 - \text{Zn}_2\text{In}_2\text{O}_5$ ) are deposited on a plastic substrate at a low  
temperature, they have an amorphous micro structure. For characteristics of the above TCO  
25 materials, see Appendix B. The amorphous structure and oxygen deficiency of the TCO allow  
the TCO coating to exhibit conductive properties and barrier properties similar to transparent  
dielectric barrier layers, such as types of silica or alumina. Because of the oxygen deficiency,  
the barrier layers gather the oxygen and keep the oxygen from passing through. Multiple thin  
layers of TCO function as a transparent electrode and a transparent barrier layer. The benefit  
30 of using TCO alternating with metallic film layers, besides the barrier properties, is that all the  
layers of the structure are conductive, thus improving conductivity.

In the preferred embodiment, a suitable apparatus for coating the substrate with  
conductive and barrier layers is illustrated schematically in FIG. 8. All of the coating  
equipment is positioned in a vacuum chamber 36. A roll of polypropylene, polyester or other  
35 suitable plastic sheet is mounted on a pay-out reel 37. Plastic sheet 38 forming the substrate  
is wrapped around a first rotatable drum 39, and fed to a take-up reel 41. A roll 42 is employed,  
as appropriate, for guiding the sheet material from the payout reel to the drum and/or to the  
take-up reel.

1 A flash evaporator 43 is mounted in proximity to the drum at a first coating station. The  
flash evaporator deposits a layer or film of monomer, typically an acrylate, on the substrate  
sheet as it travels around the drum. After being coated with a monomer, the substrate sheet  
passes an irradiation station where the monomer is irradiated by a source 44 such as an electron  
5 gun or source of ultraviolet radiation. The radiation or electron bombardment of the film  
induces polymerization of the monomer.

The sheet then preferably passes a sputtering station 46 where a coating of TCO is  
applied by magnetron sputtering. The sheet then passes another flash evaporator 47 where  
another layer of monomer is deposited over the TCO layer. Depending on whether a layer of  
10 monomer is above or below the TCO layer, either evaporator 43 or 47 is used. Clearly, if the  
TCO layer is to be sandwiched between layers of polymer, both evaporators and their respective  
radiation sources are used. In addition to magnetron sputtering, the TCO layer is processed by  
one of thermal evaporation, chemical vapor deposition, plasma enhanced chemical vapor  
deposition, and electron beam evaporation. Chemical vapor deposition is a high temperature  
15 process, and is therefore the least desirable for use with plastic substrates.

In an alternative embodiment, a liquid PML (called Liquid Multilayer, LML) smoothing  
applicator 52 is mounted in proximity to the drum at a first coating station. The liquid  
smoothing applicator deposits a layer of monomer, e.g. acrylate, over the substrate. This layer  
of monomer is cured by irradiation from an ultraviolet or electron beam source 48 adjacent the  
20 drum. Additionally, the sheet then passes sputtering station 46 where a coating of thin metal  
film, metal oxide, and/or metal nitride is applied by one of vacuum sputtering, vacuum  
metallizing, plasma assisted chemical vapor deposition, or electron beam evaporation. For  
example, silicon oxides is deposited by a plasma enhanced chemical vapor deposition process  
using a metal organic precursor and an oxidizing or inert carrier gas.

25 The various layers described are deposited in several processes in addition to vacuum  
coating techniques. For instance, the layers are deposited through nonvacuum (atmospheric)  
roll coating. Alternatively or additionally, the layers are deposited by an in line coating  
machine, whereby a conveyor belt runs the substrate to be coated past multiple coating stations.  
In a further alternative, the layers are deposited by an intermittent motion machine, that is either  
30 in a vacuum process or a nonvacuum process. In yet another alternative, the layers are coated  
using a multitude of machines. For instance, the plastic substrate is first coated through  
atmospheric roll coating with a cured polymer and subsequently coated by vacuum deposition,  
or liquid coated, such as Gravure coating.

35 For multiple layers of organic polymer coatings deposited in the PML process, take up  
reel 41, with the sheet wound thereon, functions as the pay out reel 37, and the process is  
repeated as desired by coating in both directions. The roll of sheet is removed from the vacuum  
system for use.

1           FIG. 9a illustrates a laminating process for the FPD where the coated plastic substrate and display medium are bonded together with an adhesive, pressure and temperature or through UV radiation. FIGs. 9b and 9c are a cross-sectional views of the FPD before and after undergoing the bonding process, respectively. The laminating process is one of the alternate  
5           methods for bonding the layers to construct the FPD. Because the layers of the present invention are thin; cracking, crazing, and delamination are avoided using processing methods of this type. FIGs. 9b and 9c illustrate the flat panel display with a protective overcoat 4 and the display medium 2.

          Transparent dielectric layers with good barrier properties and a high refractive index, such as metal oxides like titanium oxide or aluminum oxide, or metal nitrides such as silicon  
10           nitride or aluminum nitride, used in combination with thin, transparent metallic film layers provide a transparent conductive barrier coating. The metal oxide or metal nitride layers are deposited at specific thicknesses to optimize the optical performance (e.g. transmittance) of a particular display. Preferably, the thin metallic film layer is sandwiched in between layers of  
15           metal oxide or metal nitride. Multiple alternating layers of metal oxides or metal nitrides, with their barrier properties, and the highly conductive metallic film layers provide increased barrier performance and conductivity for a particular display medium.

          The optical and electrical performance of transparent conductive oxide coatings are also improved by mildly heating during deposition or post-annealing the coated substrate. Even  
20           though the substrate was heated to a moderate temperature of only 65°C, the resistivity of the ITO was still low enough to effectively operate as an electrode, because of the thin layer of ITO. See the Experimental Results below.

          In an alternative embodiment, a thin conductive metal nitride layer is substituted for one or more thin metallic film layers. Metal oxide or TCO layers are utilized with the metal nitride  
25           layer for enhancing both the optical and electrical performance characteristics. Metal nitrides have good gas barrier properties. However, to maintain the preferred moisture and oxygen permeability, there is a minimum thickness of the metal nitride layer. Because of the higher optical transparency silicon nitride thin films, for example, are attractive candidates for flexible FPD as barrier layers for atmospheric gases.

30           In another alternative embodiment, at least one of the metallic film layers is replaced with a polymer layer formed via the PML processes.

#### RESULTS OF CONDUCTED EXPERIMENTS

35           The plastic substrate for a flat panel display has a very low oxygen and water vapor permeability, a surface roughness much less than the barrier film thickness, a high Tg (the glass transition temperature) to allow a higher temperature and/or higher energy ITO deposition process, and a high transparency with low ND (index of refraction) birefringence.

1 Defects in the coated layers limit the barrier properties. For instance, rough substrates, particulates, and roller contact damage the coated layers. Rough substrates with thin film barriers are smoothed and prevented from damage by roller contact with an organic basecoat and polymer top coat multilayers, respectively.

5 Multiple layers of TCO's deposited on the substrate achieve lower surface resistivity than a single thick layer of TCO. Further, the multiple TCO layers act as electrodes connected in parallel. Using non-stoichiometric dielectric of a group including silicon oxides, aluminum oxides, and silicon nitrides, allow for the fabrication all efficient thin film barriers for flexible plastic films.

10 Measured data for films made of sputtered ITO exhibited exceptional barrier properties. The optical, electrical and barrier properties were measured for ITO sputter-deposited directly onto a PET substrate, and also measured with a PML acrylic base coat over the substrate before deposition of the ITO, in a roll-to-roll (web) coating process. See FIGS. 10-13, and descriptions of the Figures below. The typical performance of a single ITO layer deposited on a base coated  
15 PET substrate is  $\geq 85\%T$  (Transmittance) and  $\leq 80$  ohms/square. The ITO layer has a physical thickness of about 140 nm, for a one-half wave optical thickness, while the PET substrate has a thickness of about 0.007". For the single layer ITO film, oxygen permeability ranged from 0.005 to 0.05 oxygen cc/m<sup>2</sup>/day, while the water permeability ranged from 0.005 to 0.05 g/m<sup>2</sup>/day.

20 FIG. 10 discloses a chart showing water permeability of ITO film, as well as ITO sandwiching a silver layer, each deposited on a PET substrate versus ITO film resistance. No smoothing base coat was applied to the substrate in either case. First, the ITO layer was DC sputter deposited onto a PET substrate. The deposited ITO film is sputtered from a metal target in a web coater. The vertical lines shown connect the midpoints of the range of permeability  
25 results at each measured resistance for the ITO film sheet. The chart shows that the permeability dips to a minimal value of approximately 0.006 g/m<sup>2</sup> day at a resistance of about 60 ohms/square. The permeability reaches a maximum of approximately 0.21 g/m<sup>2</sup> day at a resistance of about 350 ohms/square. Second, for a silver layer sandwiched in between ITO film layers over the substrate, the approximate permeability range was 0.04 to 0.075 g/m<sup>2</sup> day  
30 for the sheet resistance at about 12 ohms/square.

FIG. 11 discloses a chart showing water permeability of ITO film, as well as ITO sandwiching a silver layer, each deposited on a PET substrate versus ITO film sheet thickness. First, the ITO layer alone is analyzed in the same manner as above. The chart shows that the permeability dips to a minimal value of approximately 0.006 g/m<sup>2</sup> day at a thickness of about  
35 120 nm. The permeability reaches a maximum of approximately 0.21 g/m<sup>2</sup> day at a thickness of about 40 nm. Second, for the substrate with the sandwiched silver layer, the approximate permeability range was 0.04 to 0.075 g/m<sup>2</sup> day for a sheet thickness of approximately 120 nm.

1           FIGs. 12 and 13 disclose charts showing oxygen permeability of ITO film deposited on  
a PET substrate versus ITO film sheet thickness and sheet resistivity, respectively. FIG. 12  
shows that the permeability dips to a minimal value of approximately  $0.017 \text{ g/m}^2 \text{ day}$  at a  
thickness of about 220 nm. The permeability reaches a maximum of approximately  $0.9 \text{ cc/m}^2$   
5           day at a thickness of about 40 nm.

As shown Table 1, alternating barrier layers of PML deposited organic polymers and  
dielectrics have permeation rates below the limits of the instruments, which is  $0.005 \text{ g/m}^2 \cdot \text{day}$   
for Permatran-W 3/31, an instrument for measuring water vapor transmission rates and  $0.005$   
 $\text{cc/m}^2 \cdot \text{day}$  for Ox-Tran 2/20, an instrument for measuring oxygen transmission rates.

10           A transparent dielectric barrier layer or a "single layer" of TCO deposited on the  
substrate has suitable barrier properties for the plastic FPD. The preferable barrier properties  
vary by the type of display technology: liquid crystal display (LCD) and organic light emitting  
display (OLED). The acceptable value of vapor permeation with plastic substrates for FPD  
depends on the sensitivity of the specific display technology utilized. For example, the LCD  
15           is much less sensitive to vapor permeation than the OLED. For the LCD, oxygen permeability  
is preferably in the range of about  $0.01$  to  $0.1 \text{ cc/m}^2 \cdot \text{day}$ , while water vapor permeability is  
preferably in the range of about  $0.01$  to  $0.1 \text{ g/m}^2 \cdot \text{day}$ . For OLED, permeabilities of  $\leq 0.001$   
 $\text{cc/m}^2 \cdot \text{day}$  for oxygen, and  $\leq 0.001 \text{ g/m}^2 \cdot \text{day}$  for moisture (water vapor) are preferred.

A polymer OLED and a small molecule OLED describes the two basic technologies for  
20           the layer that emits light in the OLED. For polymer OLED's, the light emitting material is  
deposited by flow coating, spin coating, gravure coating, meniscus coating, curtain coating or  
any common liquid coating or printing techniques. The small molecule OLED is normally  
thermally evaporated in a vacuum, but is also processed with nonvacuum coating methods. If  
the ITO layer is deposited by nonvacuum processes such as by screen printing, the process of  
25           the present invention is entirely nonvacuum. Alternatively, the process of the present invention  
takes place by both vacuum and nonvacuum methods. Preferably, the process takes place in  
a vacuum both to avoid contamination by particulates, and to avoid moisture and oxygen.  
Superior barrier films and other films are provided by the cleaner vacuum process.

As shown in FIGS. 10 and 11 for the LCD, as long as the sheet resistance is below about  
30            $250 \text{ ohms/square}$ , and as long as the ITO film thickness is between about 75 and 225 nm, the  
preferred water permeability for the LCD is met. As shown in FIG. 12, the preferred oxygen  
permeability for the LCD is met as long as the ITO film thickness is above about 85 nm and as  
long as the sheet resistance is below about  $150 \text{ ohm/square}$ . Because of the lower  
permeabilities preferred for the emissive displays (e.g. OLED), the barrier capability is  
35           enhanced by multilayer dielectric or TCO barriers in combination with PML processed polymer  
coatings (i.e. composite barrier layers of PML deposited organic polymer layers, dielectric  
layers and/or TCO layers).

1 Appendix D has two charts that illustrate water vapor and oxygen permeability versus ITO thickness. The measured results for semi-reactively and reactively sputtered ITO, as well as the differences between a single ITO layer and two ITO layers (with a polymer layer in between the two layers) made with a semi-reactive process, are illustrated and in tabular form.

5 'Semi-reactively' sputtered refers to DC magnetron sputtered from a ceramic target. The differences between the two processes are due to the specific process parameters, and not inherent to the process type. As shown, for the same thickness, the two ITO layers have higher conductivity and lower permeability as compared to the single ITO layer. Further, the two ITO layers have higher electrical performance, because the single ITO layer cracks and/or crazes.

10 The preferred thickness for the deposited layers is different for conductivity and barrier properties. The deposited film is thick in order to have conductive properties. Also, if a film layer is too thin it will not have adequate barrier properties. The critical thickness for these layers varies with the material and, to a lesser extent, how the layer is deposited. For ITO, the critical minimal thickness is about 20 nanometers (or 200 angstroms). The lower limits for

15 some of the metal oxides are about 10 to 30 nanometer range in packaging. Generally, 5-10 nanometers is the minimum thickness for adequate barrier properties. However, enhanced conductive properties result film thickness in the range of about 20 nanometers to 300 nanometers. If the film is thicker than that range, then the film starts cracking, and hence, loses conductivity and barrier properties. For maximizing optical transmission, it is well known that

20 optical thicknesses of thin films are selected. The typical physical thickness is 20-300 nanometers for ITO on a flexible substrate.

As seen in FIGS. 15-18, generally, regardless of the sheet resistance, the percentage of spectral transmittance and reflectance remains relatively constant. For example, at about a wavelength of 500 nm, the transmittance percentage is about 80% for resistance ranging from

25 29 ohms/square to 347 ohms/square. DC sputter deposited ITO on a hardcoated PET substrate exhibited a resistivity of 46.9 Ohms/square, which is approximately  $5 \times 10^{-4}$  ohm-cm, and a visible transmittance of 84.7%. Generally, the transmittance increases (and the reflectance decreases) as the plasma wavelength increases. There is always a compromise between high optical transmittance and high conductivity. In contrast, for FIG. 14 (a more preferred embodiment of the present invention), at the higher wavelengths, the transmittance decreases (and the reflectance increases).

30 Appendix E illustrates the Transmittance and Reflectance of semi-reactively sputtered ITO on a PET substrate for various thicknesses versus wavelength. The transmittance and reflectance of a substrate coated with a polymer layer and an ITO layer, a substrate with an ITO layer, and a substrate with two ITO layers (with a polymer layer in between the two ITO layers) are illustrated. Generally, transmittance and conductivity are inversely related. Improved optical performance is achieved by controlling the thickness and index of the polymer layers.

35



1 For a transparent electrode, conductivity varies with display technology and addressing  
method. The surface resistivity for LCD's is about 50-300 Ohm/square, and for OLED's is  
about 10-100 Ohm/square. The corresponding visible transmittance for LCD's is about 90%,  
and for OLED's is about 80-85%. The thickness of the conductor layer is compatible with the  
5 vacuum web coating processing for the flexible plastic substrate.

Table 1 shows the test results for oxygen and water vapor transmission rates of various  
samples of a substrate coated with a single ITO layer with different ohm/square coatings and  
a substrate coated with an ITO layer, a metal layer, and another ITO layer. The test conditions  
were as follows: the temperature was at 23°C/73.4°F. On each side of the barrier for the  
10 oxygen transmission rate tests, the relative humidity was 0%. On one side of the barrier for the  
water vapor transmission rate tests, the relative humidity was 100%, but the other side of the  
barrier had a relative humidity of 0%.

The first eight samples are a single layer ITO with different resistances coated onto a  
plastic substrate. For example, the '25-1' is the first sample of the resistance of 25 ohm/square;  
15 whereas '25-2' is the second sample from the same lot. The last two samples are of a substrate  
coated with an ITO layer, a metal coating, and another ITO layer, with a resistance of 10  
ohm/square. This 3 layer configuration is called "optically enhanced metal," or "induced  
transmission filter," and has similar characteristics as a single TCO layer. With the optically  
enhanced metal good conductivity, transmission and barrier properties are achieved. Preferably  
20 the ITO layers, which antireflect the metal, each have a thickness of about 30-60 nanometers.  
In several instances, the samples were tested two times. The second column for the 25 and 60  
ohm/square reflects the results of the second test.

Table 1

Sample	Water Vapor Transmission Rate (g/m <sup>2</sup> *day)		Oxygen Transmission Rate (cc/m <sup>2</sup> *day)	
25-1	0.026	<0.005 <sup>1</sup>	0.017	0.087
25-2	0.097	<0.005 <sup>1</sup>	0.584	0.257
60-1	0.042		0.059	0.071
60-2	0.050		0.204	0.090
60-3	0.007		<0.005 <sup>2</sup>	
60-4	<0.005 <sup>1</sup>		0.014	
300-1	0.243		0.861	
300-2	0.232		0.864	
M-10-1	0.076		0.035	
M-10-2	0.041		0.024	

<sup>1</sup> The actual water vapor transmission rate was at least as low as the lower limit of the instrument. Permatran-W 3/31, 0.005 g/m<sup>2</sup>\*day.

<sup>2</sup> The actual oxygen transmission rate was at least as low as the lower limit of the instrument. Ox-Tran 2/20, 0.005 cc/m<sup>2</sup>\*day.

Table 2 compares permeation rates for different coatings, including multiple dyad (an acrylate/oxide pair) layers, on polyethylene terephthalate (PET) and oriented polypropylene (OPP) substrates. As shown, a single dyad on a substrate has high permeation resistance for oxygen and moisture. In some instances, two oxygen transmission rate tests were conducted, and the results were shown in a second column. Footnote <sup>1</sup> denotes the typical permeation rate for the PET substrate.

Table 2

Sample	Water Vapor Transmission Rate (g/m <sup>2</sup> *day)	Oxygen Transmission Rate (cc/m <sup>2</sup> *day)	
2 mil PET	30.5, 272 <sup>1</sup> per micron film thickness	5.3, 1550 <sup>1</sup> per micron film thickness	
Food packaging - target values (PET/oxide)	1.55	1.5	
2 mil PET/single dyad (23°C)	<0.0078	0.03	
2 mil PET/ seven dyads (23°C)	<0.0078	<0.016	
7 mil PET/ hardcoat (23°C)	7.6		
7 mil PET/ hardcoat/ single dyad (38°C)	<0.0078, 90% Relative Humidity (RH), 100% O <sub>2</sub>	0.2682, 100% RH	0.6061, 100% RH
7 mil PET/ hardcoat/ single dyad/ ITO (38°C)	<0.0078, 90% RH, 100% O <sub>2</sub>	0.0098, 100% RH	0.0128, 100% RH
PET/oxide	0.7-1.5	0.15-0.9	
PET/Al	0.6	0.17	
OPP, copolymer, 1 mil	1800	1.3	
OPP/ oxide	17-546	0.08-0.4	
OPP/Al	20	0.11	

Table 3

Sample	Water Vapor Transmission Rate (g/100in <sup>2</sup> *24 hours)	Oxygen Transmission Rate (cc/100in <sup>2</sup> *24 hours)
A	<0.001	<0.001
B	<0.001	<0.001
C	<0.001	<0.001
D	<0.001	<0.001
E	0.369	1.971
F	0.370	1.934
G	0.340	1.834
H	0.377	1.888

Samples A through D are layers of polymer (PML)/oxide/polymer (PML) on 2 mil PET. Samples E through H are 2 mil PET only.

Although the present invention has been described and is illustrated with respect to various embodiments thereof, it is to be understood that it is not to be so limited, because changes and modifications may be made therein which are within the full intended scope of this invention as hereinafter claimed. In particular, the structure disclosed for flat panel displays is also used with other display technologies, such as polymer light emitting diode (PLED) and light emitting diode (LED) displays.

## 1 CLAIMS

1. A composite substrate for use in flat panel displays, packaging or electro luminescence lamps comprising:  
5 a plastic substrate; and  
a first conductive barrier material deposited over the plastic substrate, the conductive barrier material including one of a thin transparent conductive oxide, and a metal nitride.
- 10 2. The composite substrate of claim 1 further comprising a first organic polymer deposited over the plastic substrate.
3. The composite substrate of claim 1 further comprising a first organic polymer deposited over the conductive barrier layer.
- 15 4. The composite substrate of claim 2 further comprising a second organic polymer deposited over the conductive barrier layer.
5. The composite substrate of claim 1 further comprising one or more additional  
20 layers of conductive barrier material deposited over the plastic substrate, the additional layers of conductive barrier material having the same material as the first conductive barrier material.
6. The composite substrate of claim 5 further comprising one or more additional  
25 layers deposited over the previously deposited conductive barrier material layer, respectively, each additional layer including one of an organic polymer, a thin transparent dielectric, a thin transparent metallic film and a thin transparent conductive oxide.
7. The composite substrate of claim 1 wherein the thin transparent metallic film is  
30 aluminum.
8. The composite substrate of claim 1 wherein the thin transparent metallic film is silver.
9. The composite substrate of claim 1 wherein the plastic substrate is one of a  
35 polyester and a polyolefin.
10. The composite substrate of claim 1 wherein the transparent conductive oxide coating is tin doped indium oxide.

- 1           11.    The composite substrate of claim 1 wherein the transparent dielectric barrier is one of silicon oxide and aluminum oxide.
- 5           12.    The composite substrate of claim 11 wherein the aluminum oxide is deposited by one of evaporation of the aluminum which is then converted to an oxide in an oxygen plasma and electron beam evaporation.
- 10          13.    The composite substrate of claim 1 wherein the dielectric layer is deposited by a plasma assisted chemical vapor deposition process using one of an oxidizing carrier gas and inert carrier gas.
14.    The composite substrate of claim 7 wherein the aluminum layer is deposited by one of vacuum metallizing and sputtering.
- 15          15.    The composite substrate of claim 1 further comprising multiple alternating layers of vapor deposited crosslinked organic monomer, and transparent conductive oxide.
16.    An apparatus for fabricating a composite substrate for use in flat panel display packaging comprising one of a roll coater, a vacuum coater, an in line coating machine and an intermittent motion machine and a Gravure coating machine.
- 20          17.    The apparatus of claim 16 wherein the substrate is coated using more than one apparatus.
- 25          18.    A process for fabricating a composite substrate for use in flat panel display packaging comprising:  
                providing a plastic substrate; and  
                depositing a first conductive barrier material over the plastic substrate, the conductive barrier material including one of a thin transparent conductive oxide, and a metal nitride.
- 30          19.    The process of claim 18 further comprising depositing a first organic polymer over the plastic substrate.
- 35          20.    The process of claim 18 further comprising depositing a first organic polymer over the conductive barrier layer.

- 1           21.    The process of claim 19 further comprising depositing a second organic polymer  
over the conductive barrier layer.
- 5           22.    The process of claim 18 further comprising depositing one or more additional  
layers of conductive barrier material over the plastic substrate, the additional layers of  
conductive barrier material having the same material as the first conductive barrier material.
- 10          23.    The composite substrate of claim 22 further comprising depositing one or more  
additional layers over the previously deposited conductive barrier material layer, respectively,  
each additional layer including one of an organic polymer, a thin transparent dielectric, a thin  
transparent metallic film and a thin transparent conductive oxide.
- 15          24.    The process of claim 19 further comprising vapor depositing and crosslinking an  
organic monomer to form the polymer layer.
- 20          25.    The process of claim 19 further comprising liquid smoothing an organic polymer  
to form the polymer layer.
- 25          26.    The process of claim 19 further comprising depositing the polymer layer over the  
previously deposited layer before the previously deposited layer contacts a surface.
- 30          27.    The process of claim 18 wherein the thin transparent metallic film is aluminum.
28.    The process of claim 18 wherein the thin transparent metallic film is silver.
29.    The process of claim 18 wherein the plastic substrate is one of a polyester and a  
polyolefin.
30.    The process of claim 18 wherein the transparent conductive oxide coating is tin  
doped indium oxide.
31.    The process of claim 18 wherein the transparent dielectric barrier is one of silicon  
oxide and aluminum oxide.
- 35          32.    The process of claim 31 further comprising depositing the aluminum oxide by one  
of evaporation of the aluminum which is then converted to an oxide in an oxygen plasma and  
electron beam evaporation.

1           33     The process of claim 18 further comprising depositing the dielectric layer by a plasma assisted chemical vapor deposition process using one of an oxidizing carrier gas and inert carrier gas.

5           34.    The process of claim 27 further comprising depositing the aluminum layer by one of vacuum metallizing and sputtering.

          35.    The process of claim 18 wherein the transparent conductive oxide is deposited by sputtering.

10           36.    The process of claim 35 further comprising providing hydrogen in a plasma of a vacuum chamber used in the sputtering process of the transparent conductive oxide.

          37.    The process of claim 18 further comprising mildly annealing the substrate before deposition of layers thereon.

15           38.    The process of claim 37 wherein the substrate is annealed to approximately 65°C.

20

25

30

35



## AMENDED CLAIMS

[received by the International Bureau on 25 April 2000 (25.04.00);  
original claims 1-3, 5, 8, 11-16, 18-22, 24-29, 31-34 and 36 amended;  
original claims 37 and 38 cancelled; new claims 37-41 added;  
remaining claims unchanged (5 pages)]

1. A composite substrate for use in one of displays, packaging and electro luminescence lamps comprising:
- 5       a plastic substrate;
- a first conductive barrier material deposited over the plastic substrate, the conductive barrier material including one of a thin transparent conductive oxide, a thin transparent metal and a thin transparent metal nitride; and
- a first organic polymer deposited over the conductive barrier material.
- 10
2. A composite substrate for use in one of displays, packaging and electro luminescence lamps comprising:
- a substrate;
- a first organic polymer deposited over the substrate; and
- 15       a first conductive barrier material deposited over the first organic polymer layer, the conductive barrier material including one of a thin transparent conductive oxide, a thin transparent metal and a thin transparent metal nitride.
3. The composite substrate of claim 1 further comprising a second organic polymer deposited over the plastic substrate, in between the substrate and the conductive barrier layer.
- 20
4. The composite substrate of claim 2 further comprising a second organic polymer deposited over the conductive barrier layer.
- 25
5. The composite substrate of claim 1 further comprising one or more additional layers of conductive barrier material deposited over the first organic polymer layer, the additional layers of conductive barrier material having the same material as the first conductive barrier material.
- 30
6. The composite substrate of claim 5 further comprising one or more additional layers deposited over the previously deposited conductive barrier material layer, respectively, each additional layer including one of an organic polymer, a thin transparent dielectric, a thin transparent metallic film and a thin transparent conductive oxide.
- 35
7. The composite substrate of claim 1 wherein the thin transparent metallic film is aluminum.

- 1           8.    The composite substrate of claim 1 wherein the thin transparent metallic film is one of silver, gold, a silver alloy and a gold alloy.
- 5           9.    The composite substrate of claim 1 wherein the plastic substrate is one of a polyester and a polyolefin.
10.   The composite substrate of claim 1 wherein the transparent conductive oxide coating is tin doped indium oxide.
- 10          11.   The composite substrate of claim 1 further comprising a first transparent dielectric barrier which is one of silicon oxide and aluminum oxide.
12.   The composite substrate of claim 11 wherein the aluminum oxide is deposited by one of thermal evaporation of and electron beam evaporation of the aluminum which is then  
15 converted to an oxide by an oxygen containing plasma.
13.   The composite substrate of claim 11 wherein the dielectric layer is deposited by a plasma assisted chemical vapor deposition process.
- 20          14.   The composite substrate of claim 8 wherein the metallic layer is deposited by one of vacuum metallizing and sputtering.
15.   The composite substrate of claim 1 further comprising multiple alternating layers of deposited crosslinked organic monomer, and transparent conductive oxide.
- 25          16.   An apparatus for fabricating a composite substrate for use in one of display fabrication and packaging comprising at least one of a roll coater, a vacuum coater, an in-line coating machine and an intermittent motion machine, and a Gravure coating machine.
- 30          17.   The apparatus of claim 16 wherein the substrate is coated using more than one apparatus.
18.   A process for fabricating a composite substrate for use in one of display fabrication and packaging comprising:  
35            providing a substrate;  
            depositing a first conductive barrier material over the substrate, the conductive barrier material including one of a thin transparent conductive oxide, a thin transparent metallic film and a thin conductive metal nitride; and

1                    depositing a first organic polymer over the first conductive barrier layer.

19.    The process of claim 18 further comprising depositing a second organic polymer  
5           over the substrate, in between the substrate and the first conductive barrier material.

20.    The process of claim 19 further comprising depositing one or more additional  
         layers of conductive barrier material over the first organic polymer layer, the additional layers  
         of conductive barrier material having the same material as the first conductive barrier material.

10       21.    The process of claim 20 further comprising depositing one or more additional  
         layers over the previously deposited conductive barrier material layer, respectively, each  
         additional layer including one of an organic polymer, a thin transparent dielectric, a thin  
         transparent metallic film and a thin transparent conductive oxide.

15       22.    The process of claim 18 further comprising depositing one or more additional  
         layers of conductive barrier material over the first organic polymer layer, the additional layers  
         of conductive barrier material having the same material as the first conductive barrier material.

20       23.    The composite substrate of claim 22 further comprising depositing one or more  
         additional layers over the previously deposited conductive barrier material layer, respectively,  
         each additional layer including one of an organic polymer, a thin transparent dielectric, a thin  
         transparent metallic film and a thin transparent conductive oxide.

25       24.    The process of claim 18 further comprising depositing and crosslinking an organic  
         monomer in one of a vacuum and a plasma to form the polymer layer.

25.    The process of claim 18 wherein the substrate is a plastic substrate, the process  
         further comprising smoothing the plastic substrate by depositing a polymer which is liquid  
         coated over the substrate.

30       26.    The process of claim 18 further comprising depositing the polymer layer over the  
         previously deposited layer before the previously deposited layer contacts a surface.

27.    The process of claim 18 wherein the thin transparent metallic film is one of silver,  
35           gold, a silver alloy and a gold alloy.

28.    The process of claim 18 wherein the thin transparent metallic film is aluminum.

1           29.    The process of claim 18 wherein the substrate contains one of at least a polyester  
and a polyolefin.

5           30.    The process of claim 18 wherein the transparent conductive oxide coating is tin  
doped indium oxide.

          31.    The process of claim 18 further comprising depositing a first transparent  
dielectric barrier which is one of silicon oxide and aluminum oxide.

10          32.    The process of claim 31 wherein the aluminum oxide is made by one of thermal  
evaporation of and electron beam evaporation of the aluminum which is then converted to an  
oxide by an oxygen containing plasma.

15          33.    The process of claim 18 wherein the transparent conductive oxide layer is  
deposited by a plasma assisted chemical vapor deposition process.

          34.    The process of claim 18 wherein the metallic film layer is deposited by one of  
vacuum metallizing and sputtering.

20          35.    The process of claim 18 wherein the transparent conductive oxide is deposited by  
sputtering.

25          36.    The process of claim 35 wherein in the sputtering process of the transparent  
conductive oxide, hydrogen is provided in the plasma.

          37.    The composite substrate of claim 1 wherein the transparent conductive oxide  
coating contains indium.

30          38.    The composite substrate of claim 1 further comprising one or more additional  
layers of conductive barrier material deposited over the plastic substrate, the additional layers  
of conductive barrier material having material that is different than that of the first conductive  
barrier material.

35          39.    The process of claim 18 wherein the transparent conductive oxide coating  
contains indium.

1           40. A composite substrate for use in one of displays, packaging and electro  
luminescence lamps comprising:

          a plastic substrate; and

5           a first optically enhanced layer deposited over the plastic substrate, wherein the  
optically enhanced layer has one of a metal and a metal nitride layer sandwiched between two  
thin transparent conductive oxide layers.

10          41. The composite substrate of claim 40 wherein a second optically enhanced layer  
is deposited over the first optically enhanced layer, wherein the second optically enhanced layer  
has the same material as the first optically enhanced layer.

15

20

25

30

35

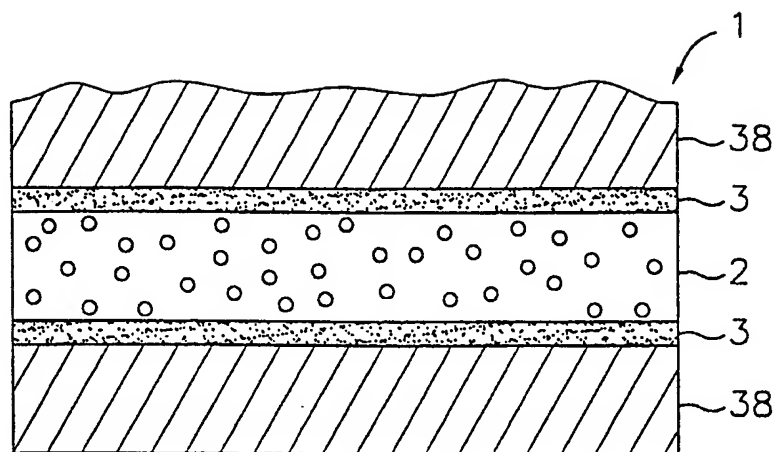


FIG. 1

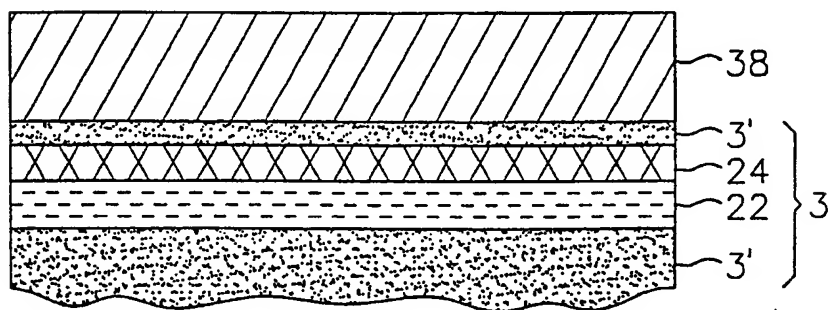


FIG. 2

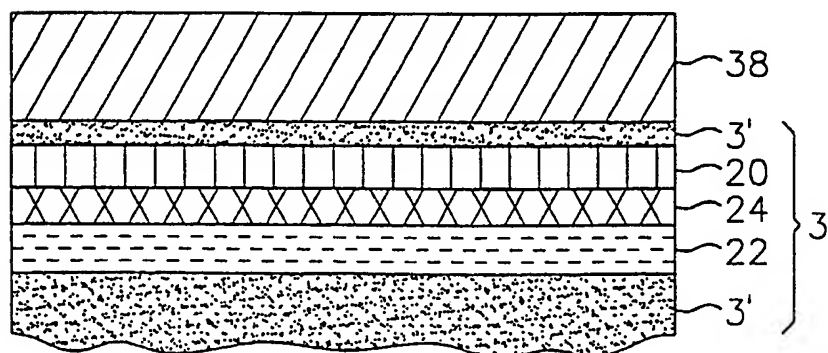


FIG. 3

2/19

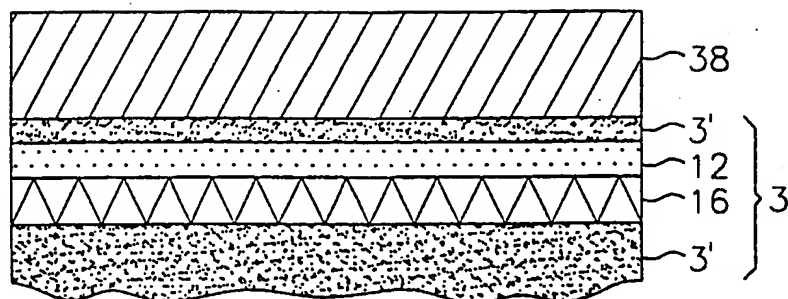


FIG. 4

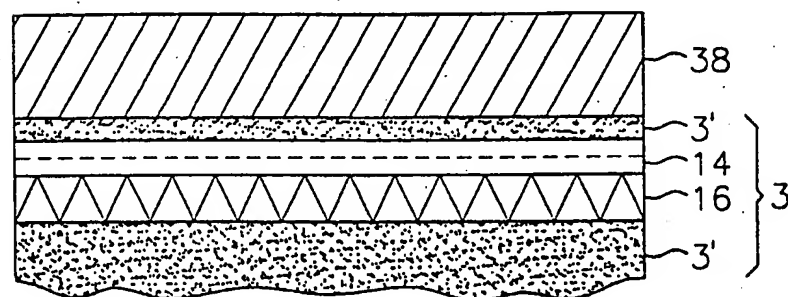


FIG. 5

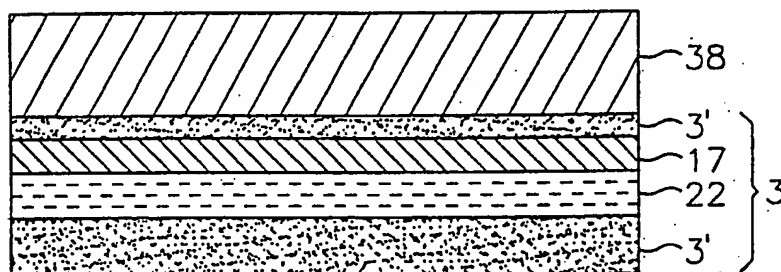


FIG. 6

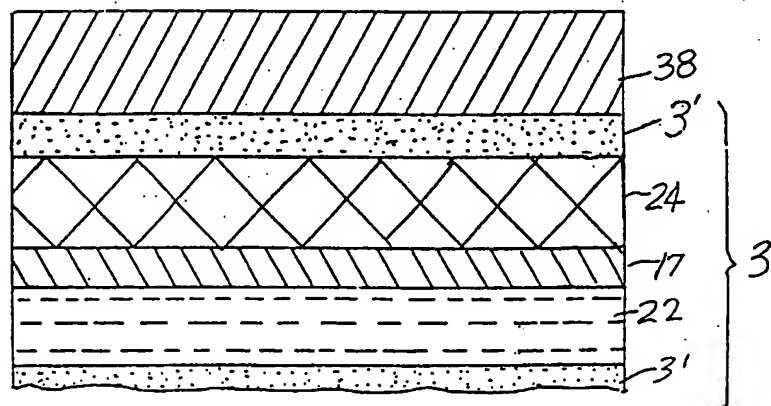
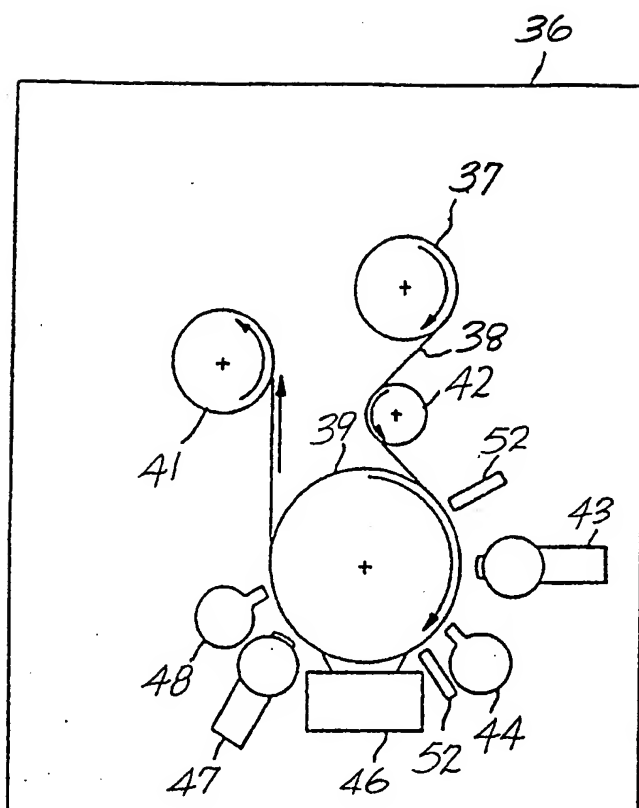
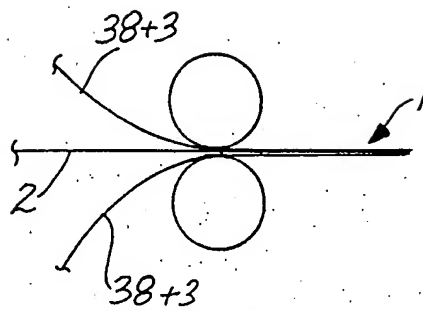


Fig. 7



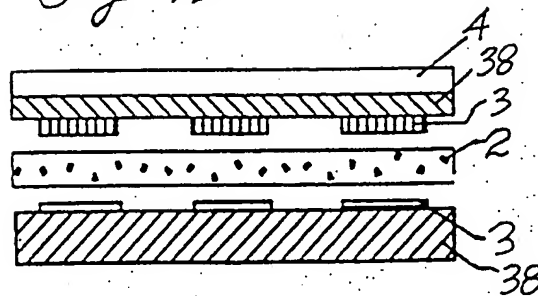
*Fig. 8*



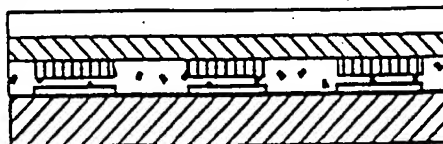


*Fig. 9a*

*Fig. 9b*

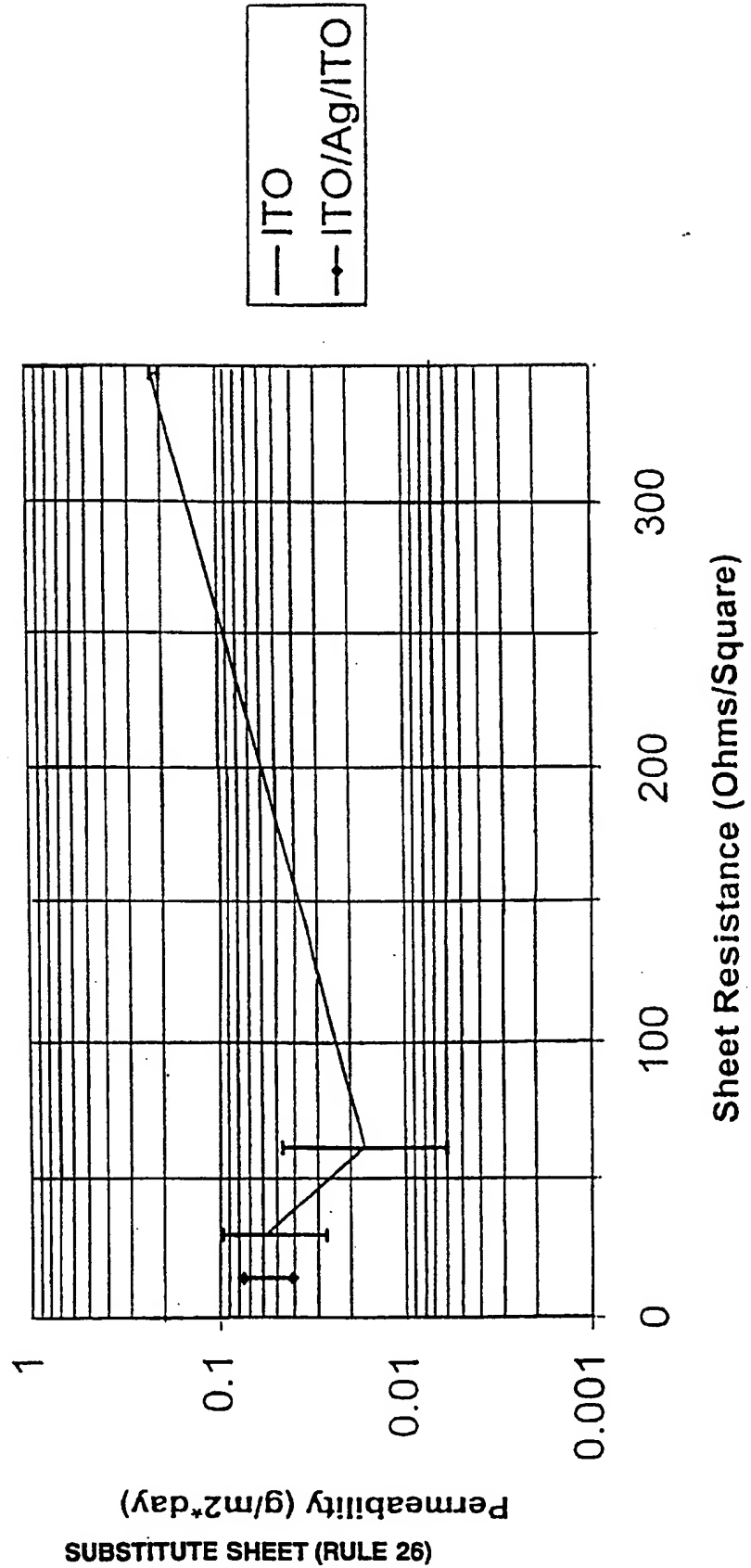


*Fig. 9c*



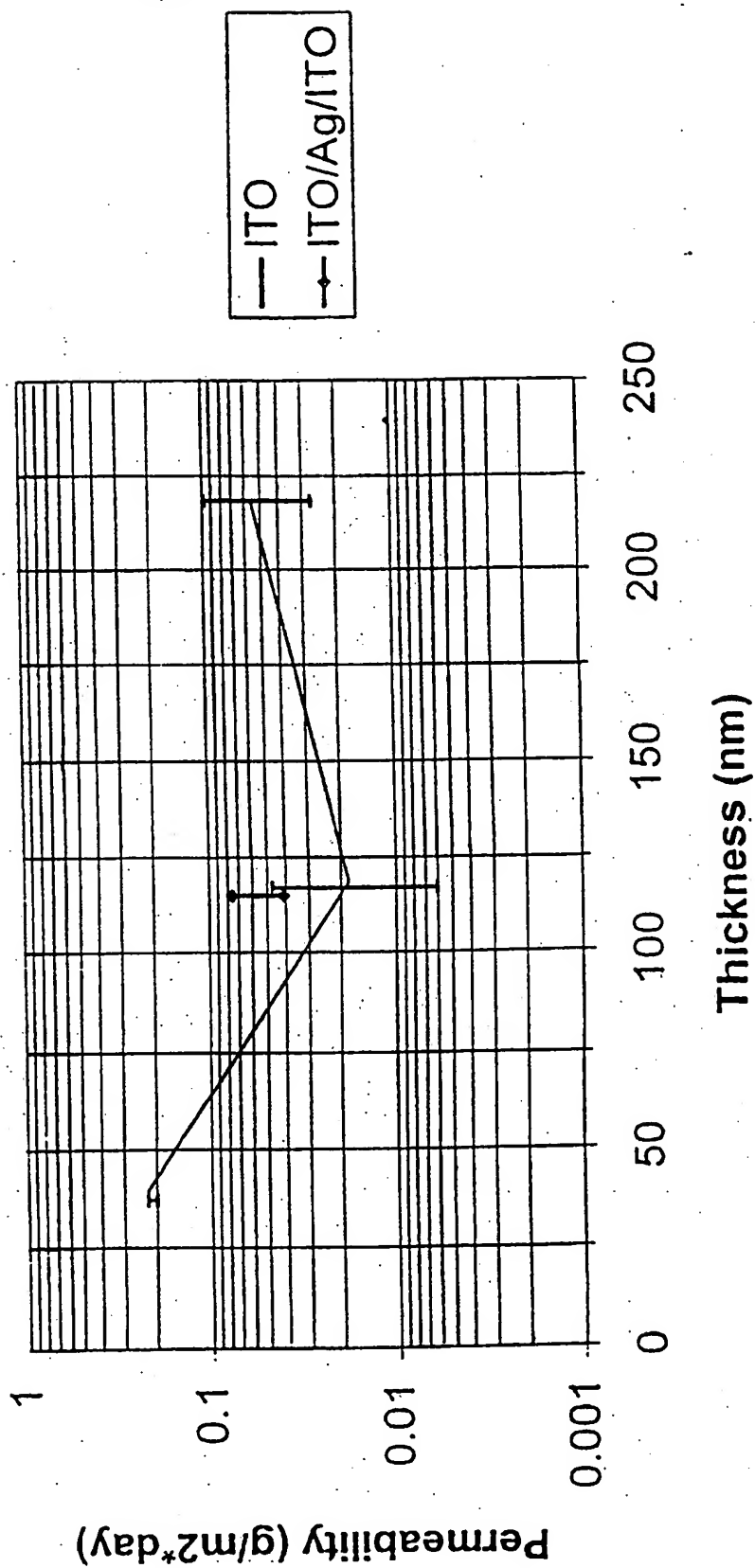
5/19

*Fig. 10*

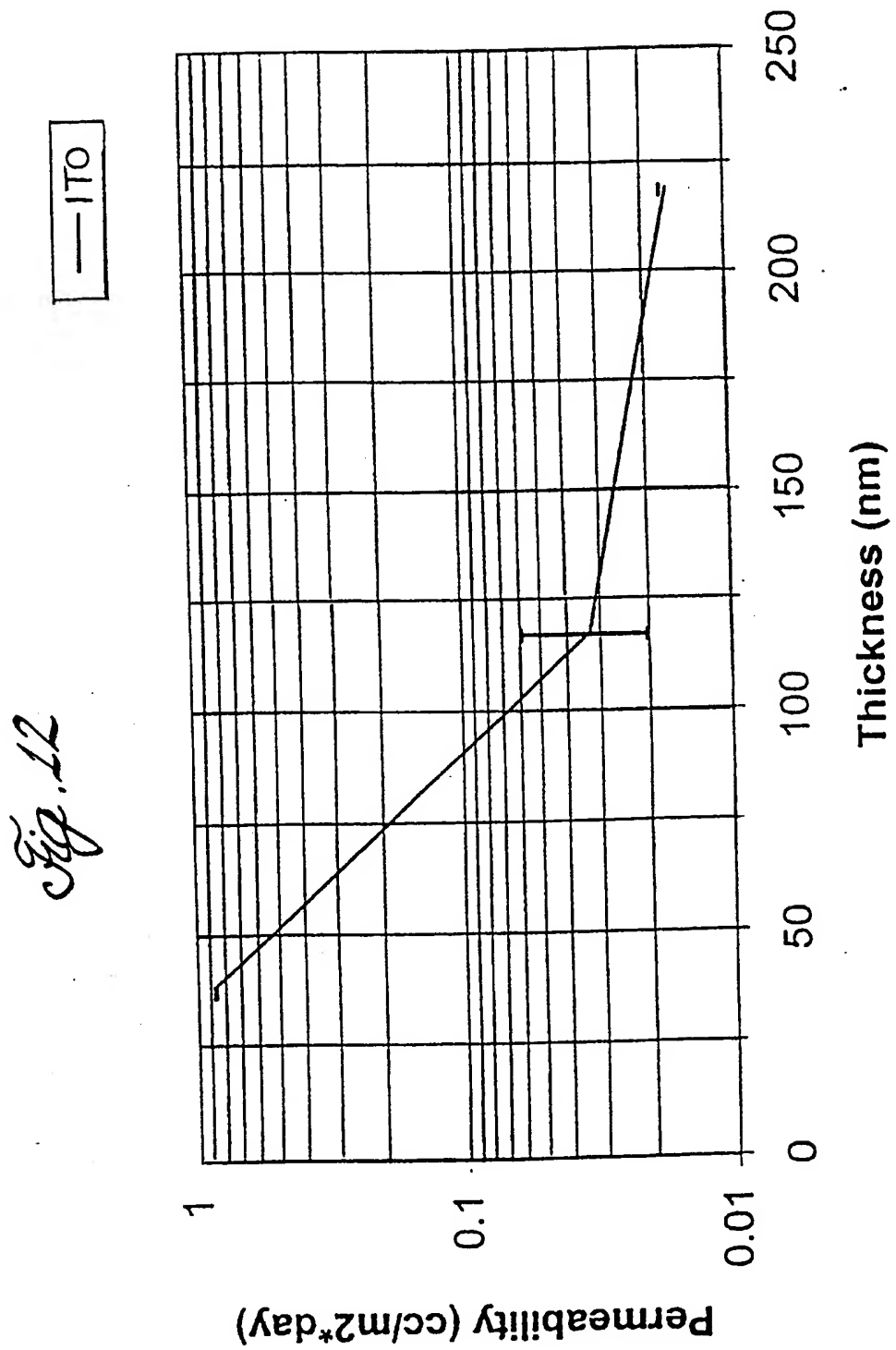


6/19

*Fig. 11*

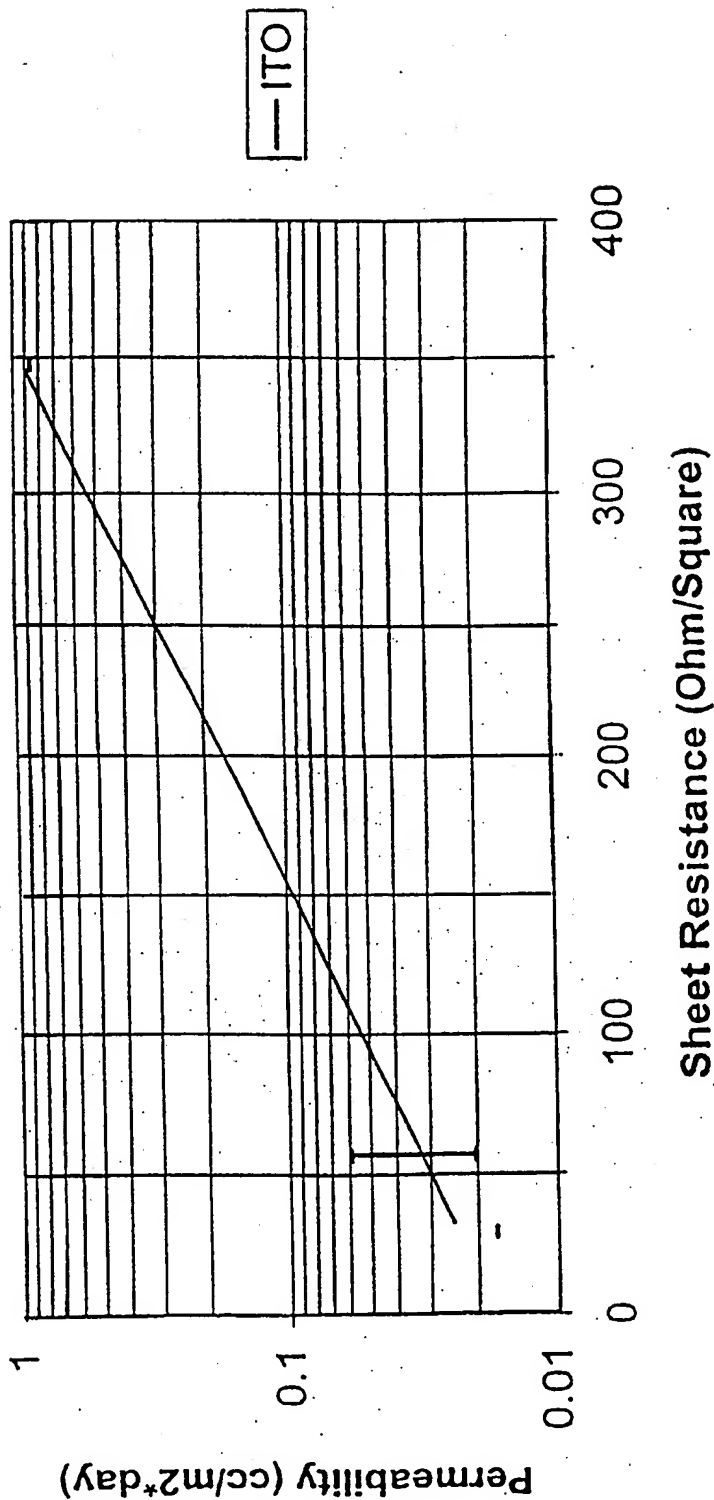


7/19



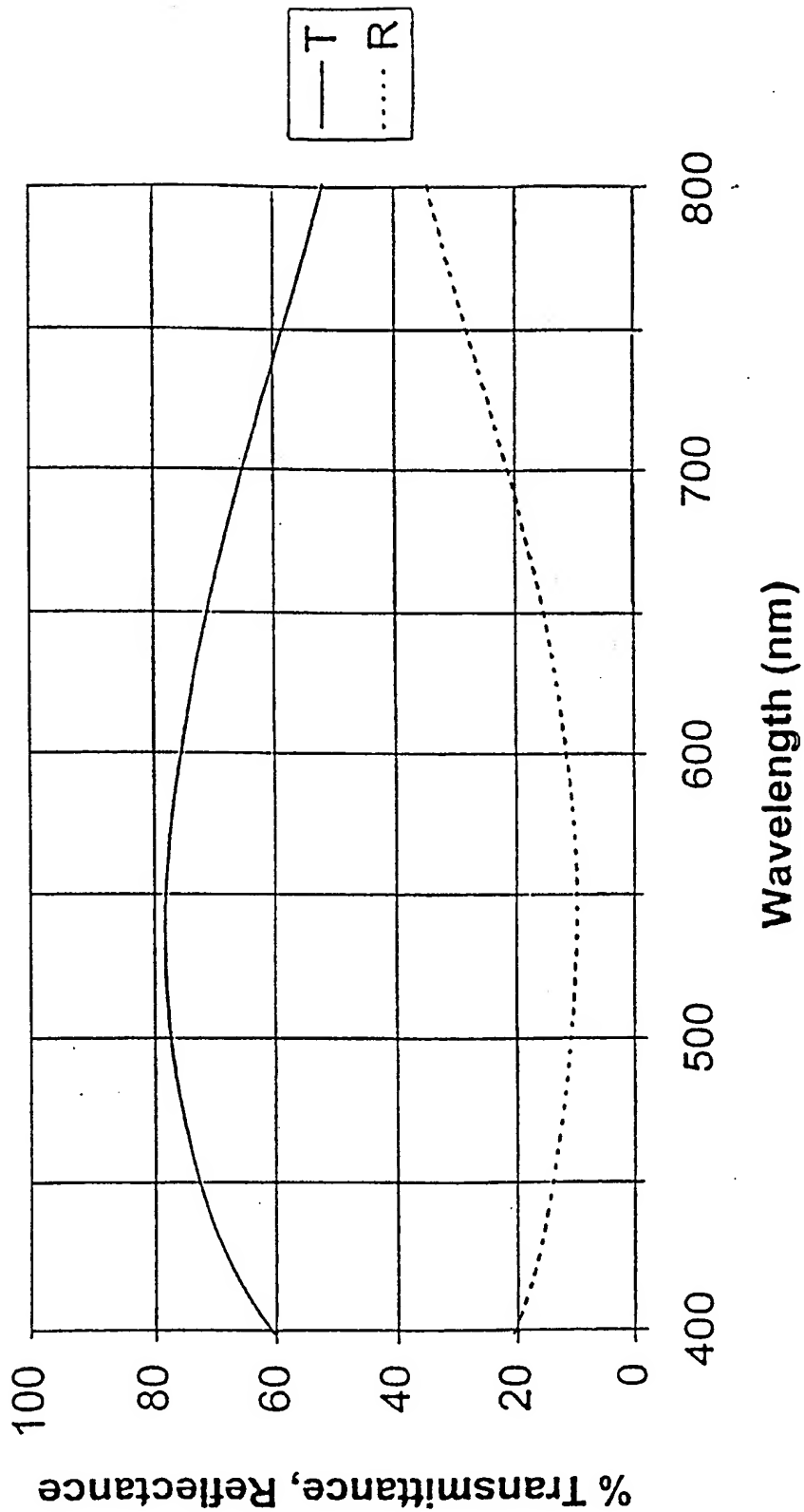
8/19

Fig. 13



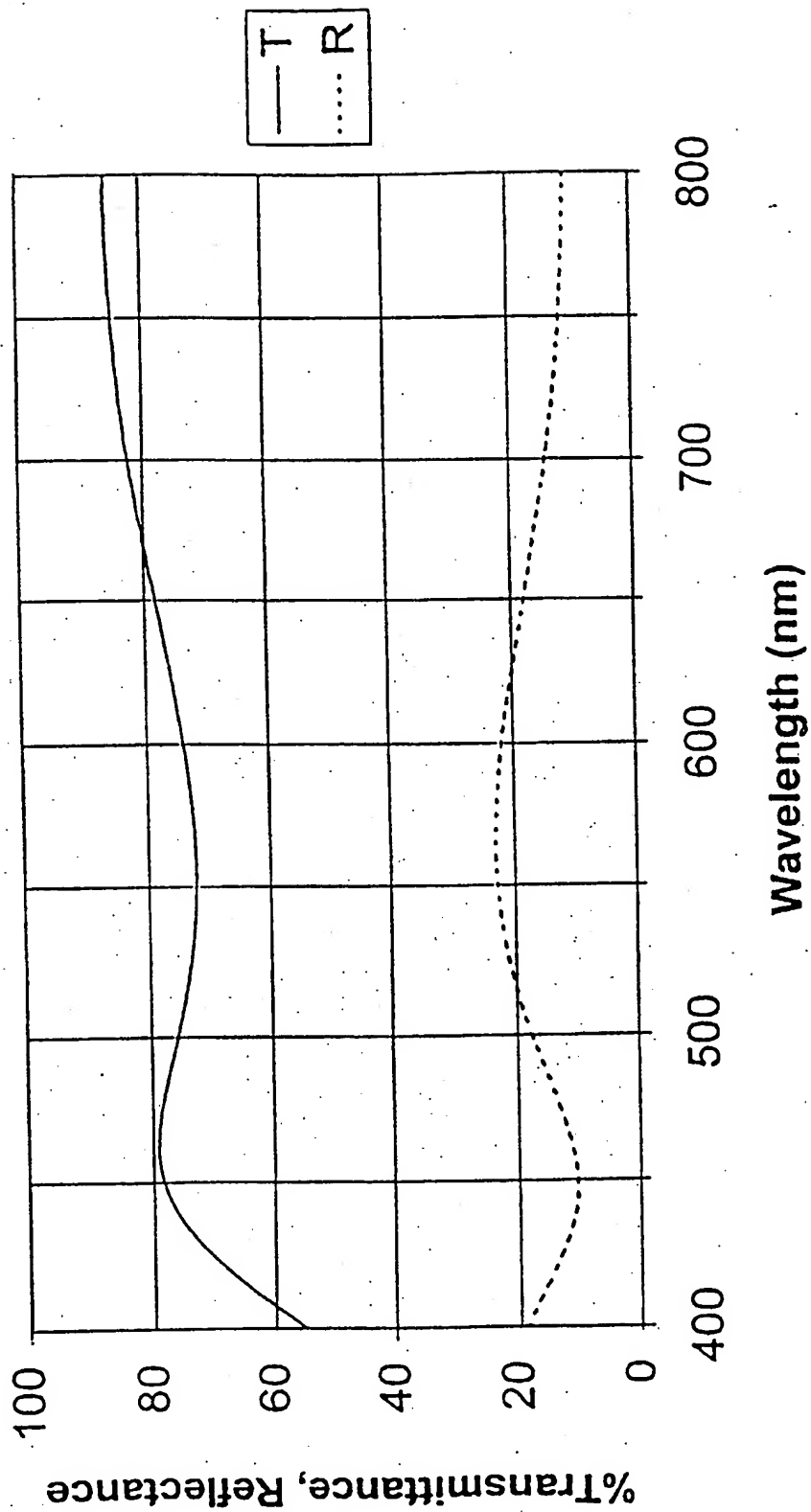
9/19

*Fig. 14*



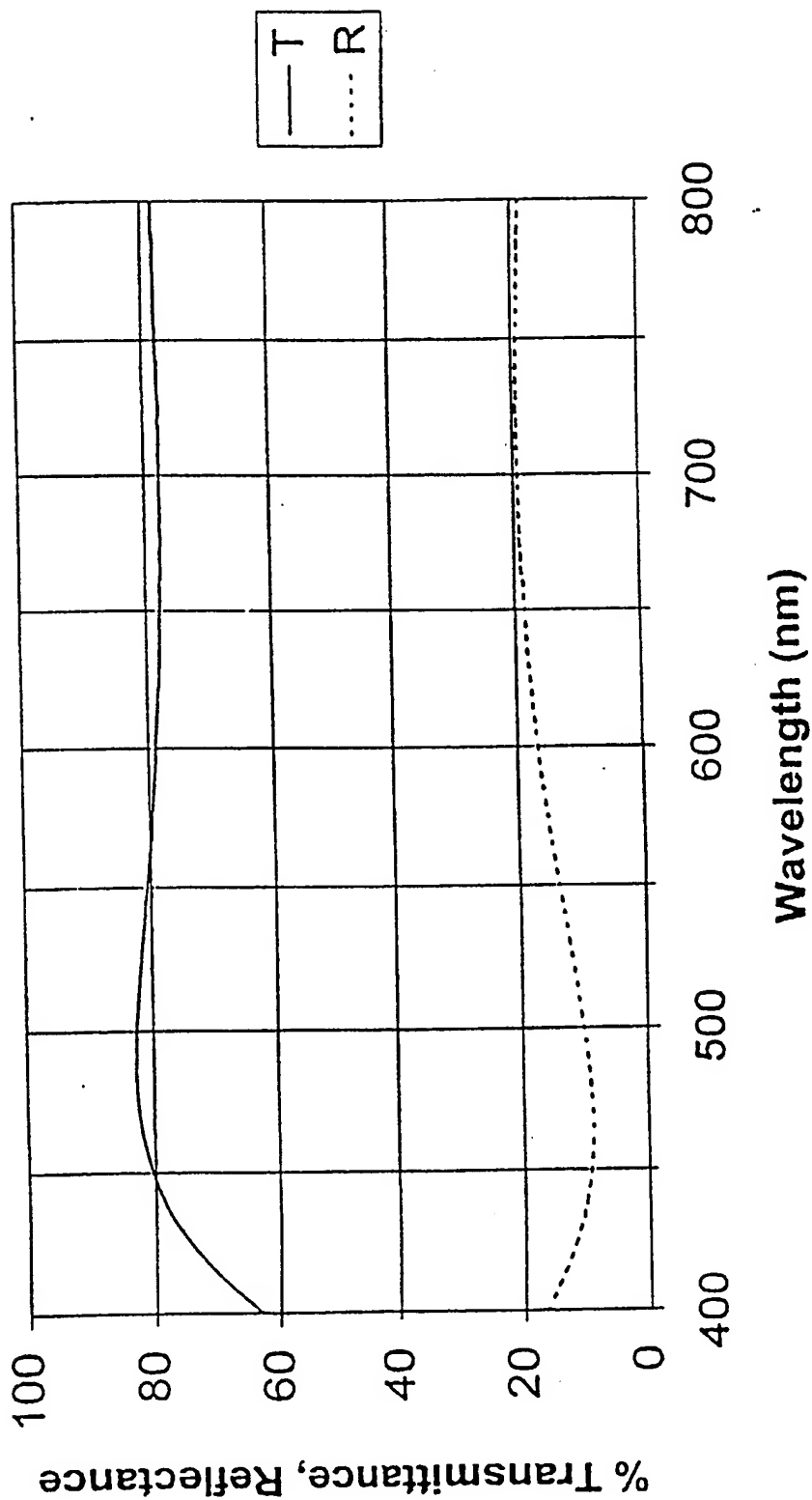
10/19

*Fig. 15*



11/19

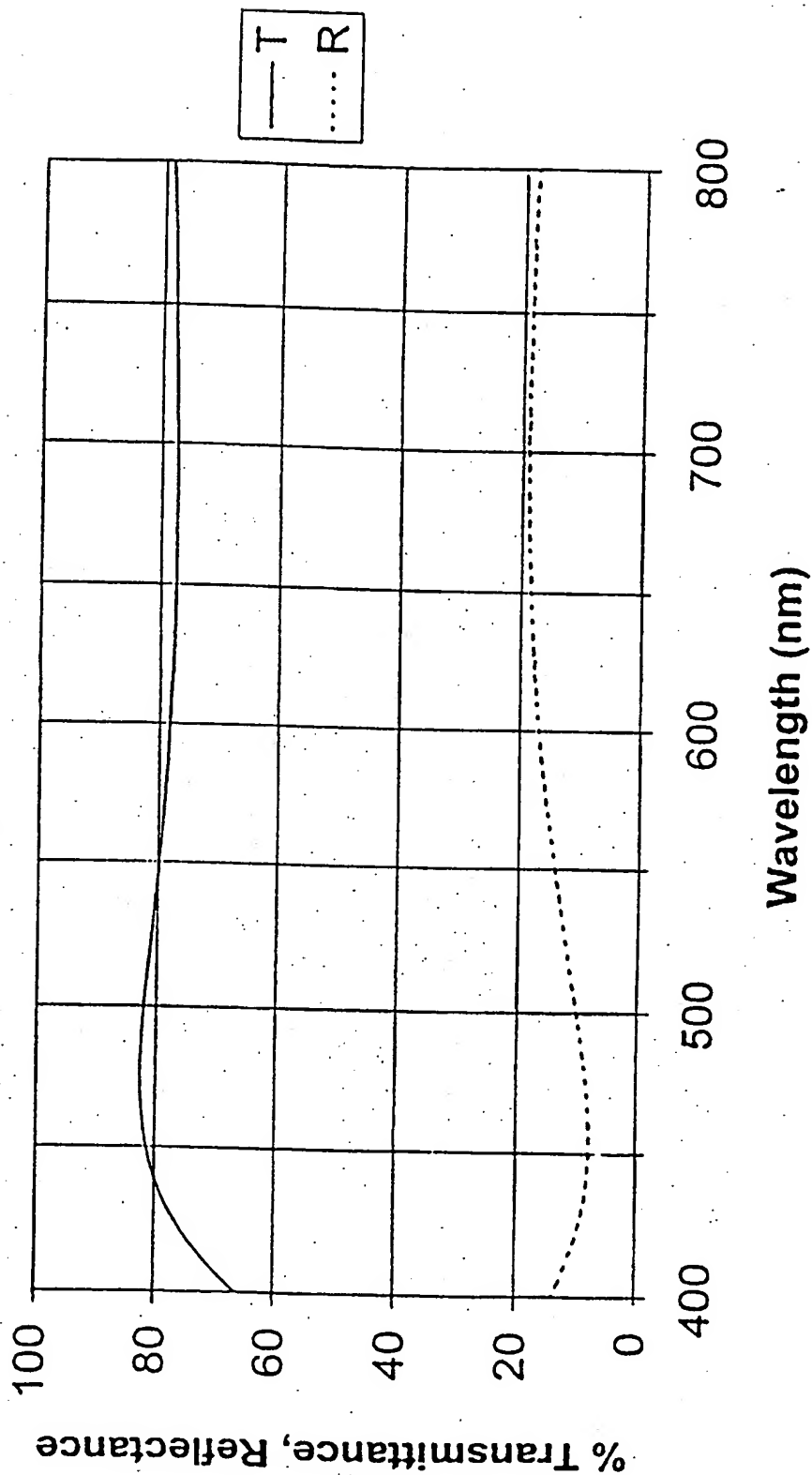
*Fig. 16*





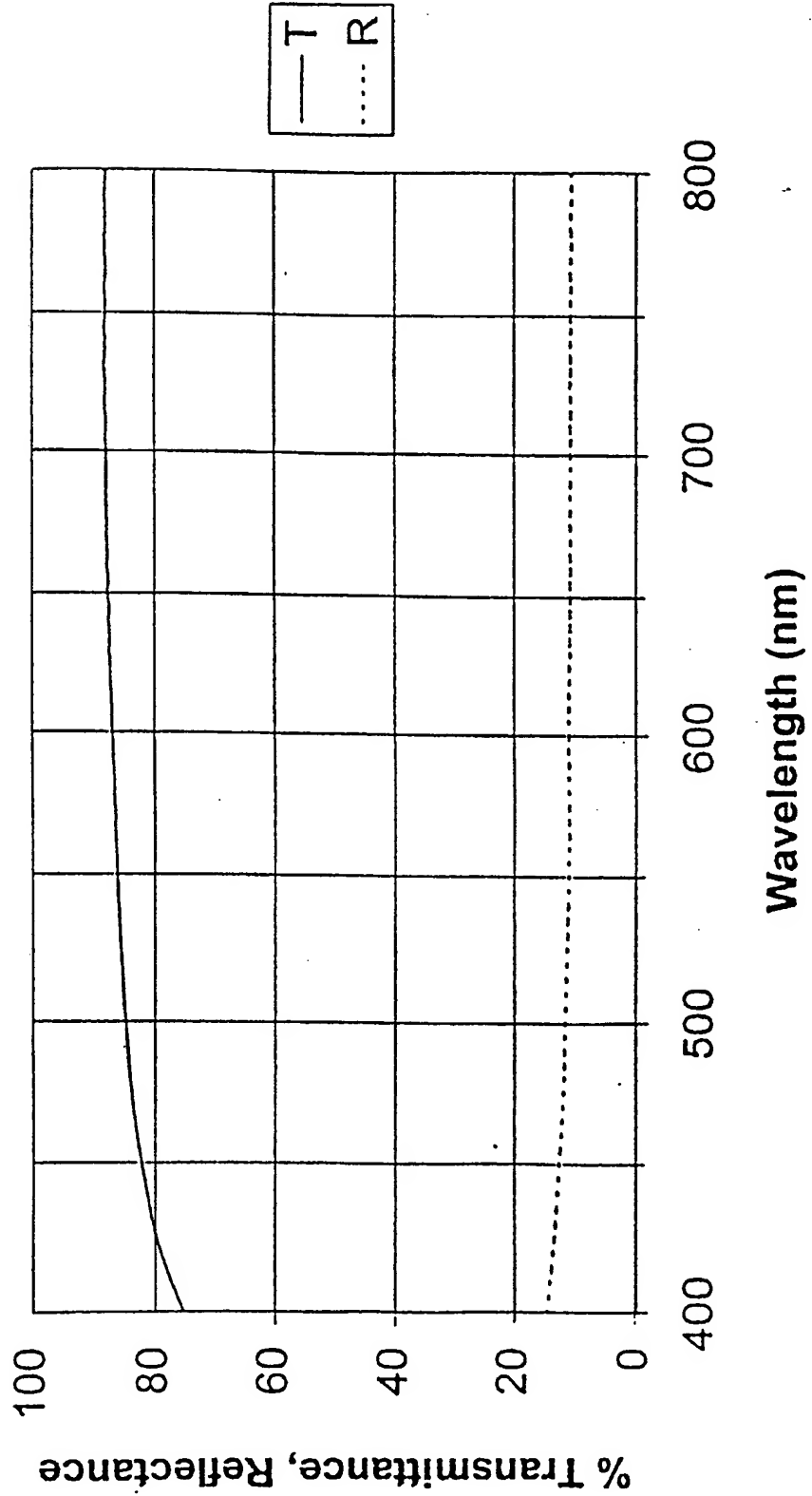
12/19

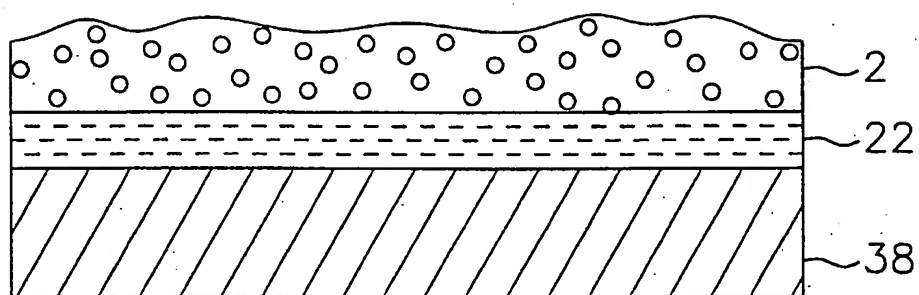
*Fig. 17*



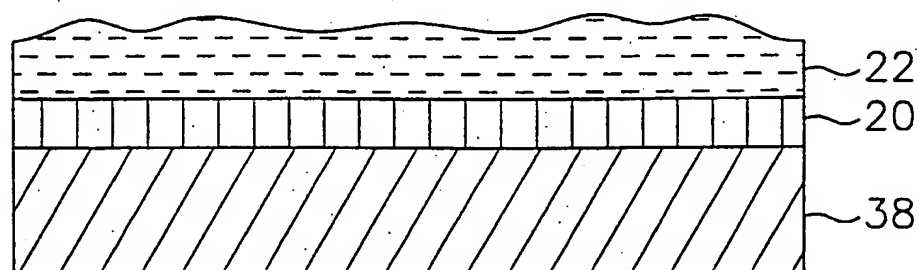
13/19

*Fig. 1B*

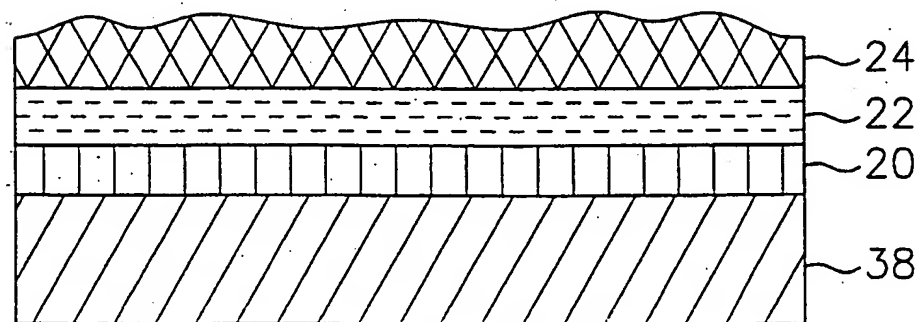




*FIG. 19*



*FIG. 20*



*FIG. 21*

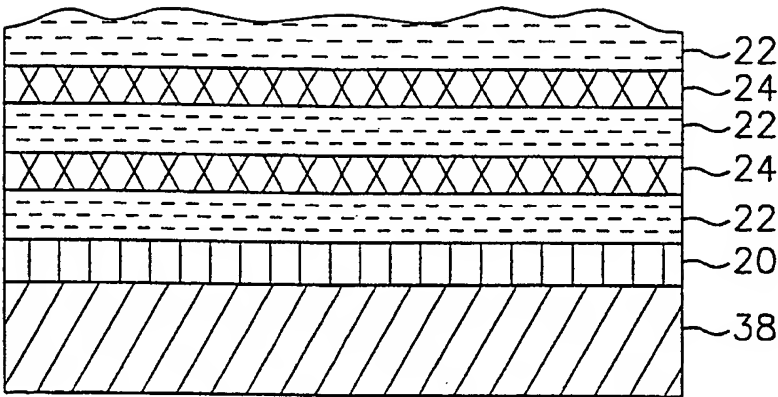


FIG. 22

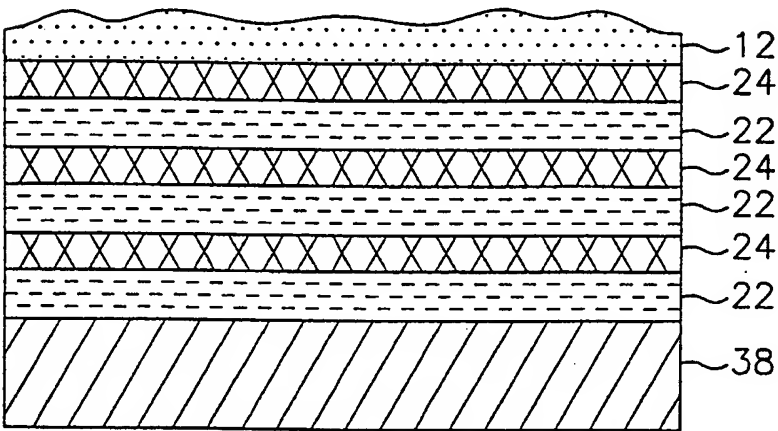


FIG. 23

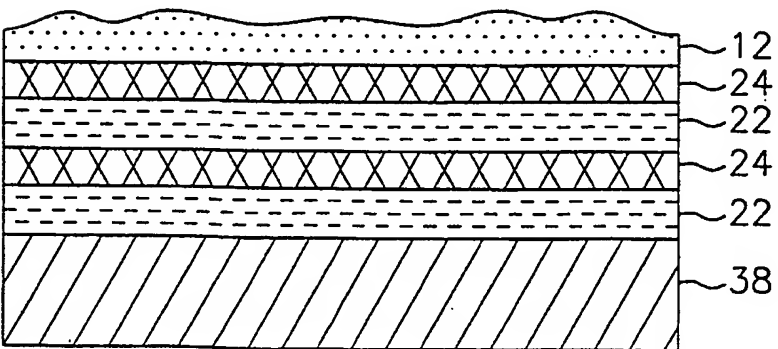
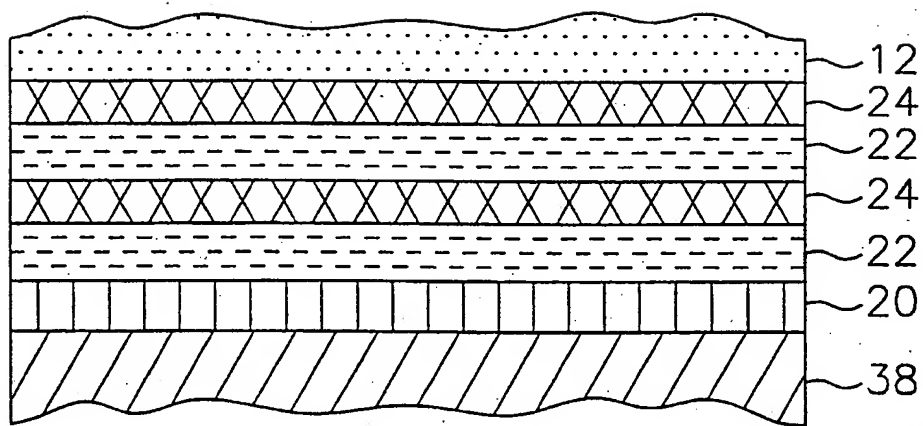
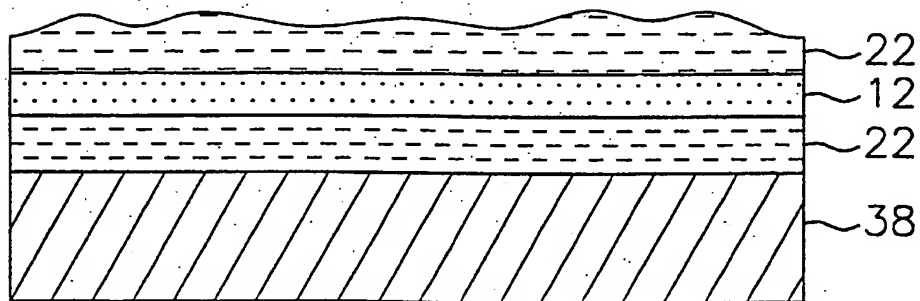


FIG. 24



**FIG. 25**



**FIG. 26**

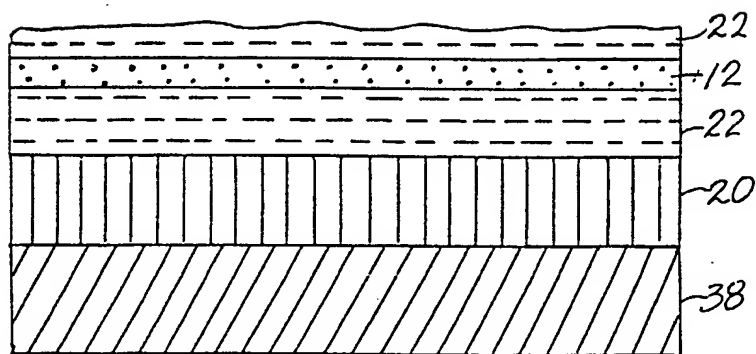


FIG. 27

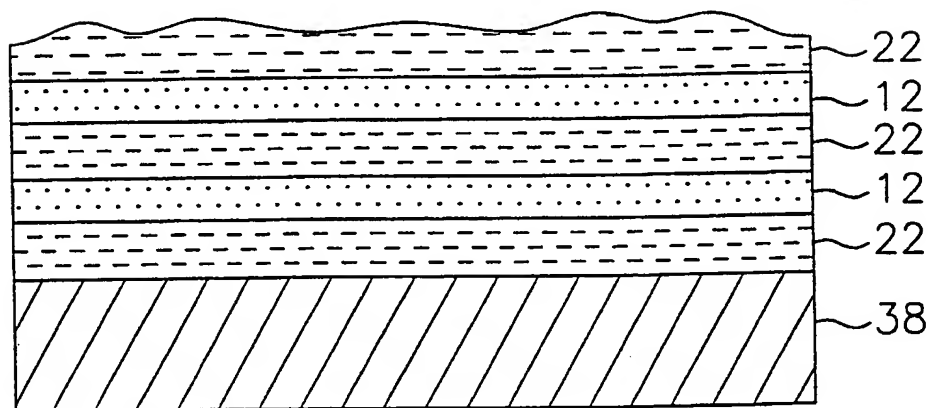


FIG. 28

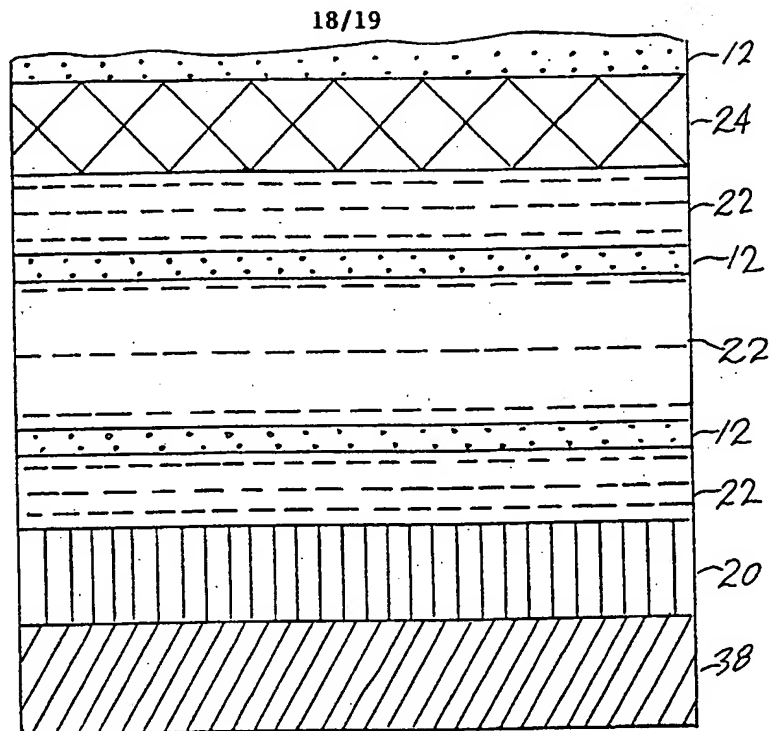


FIG. 29

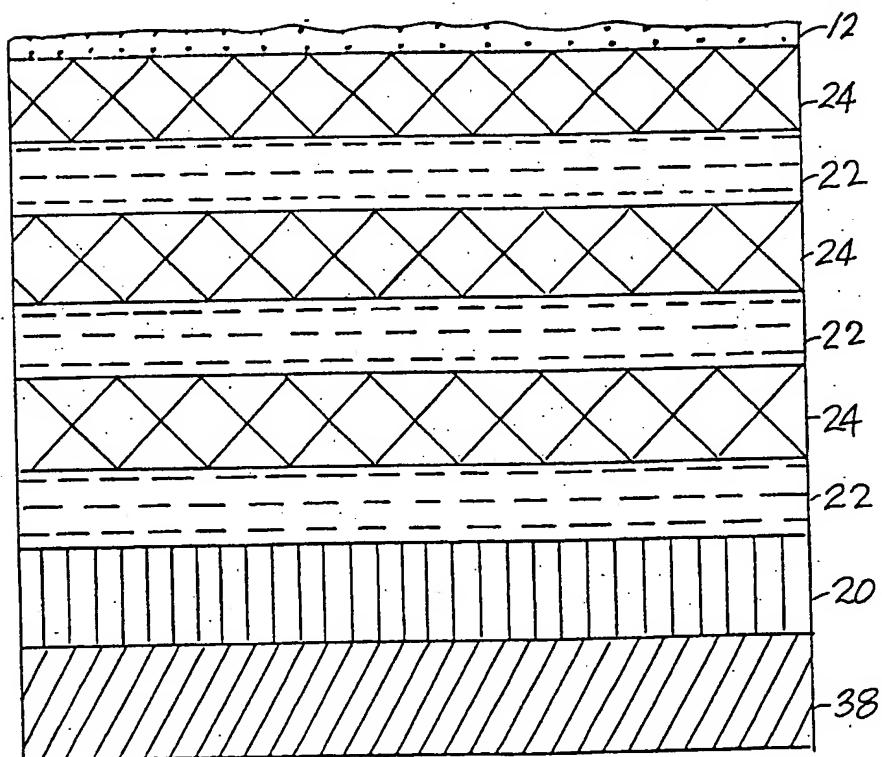
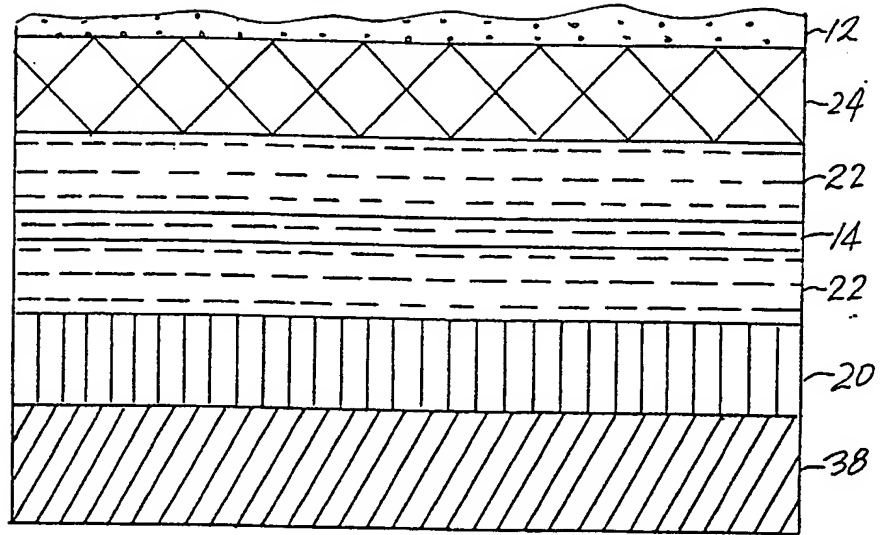
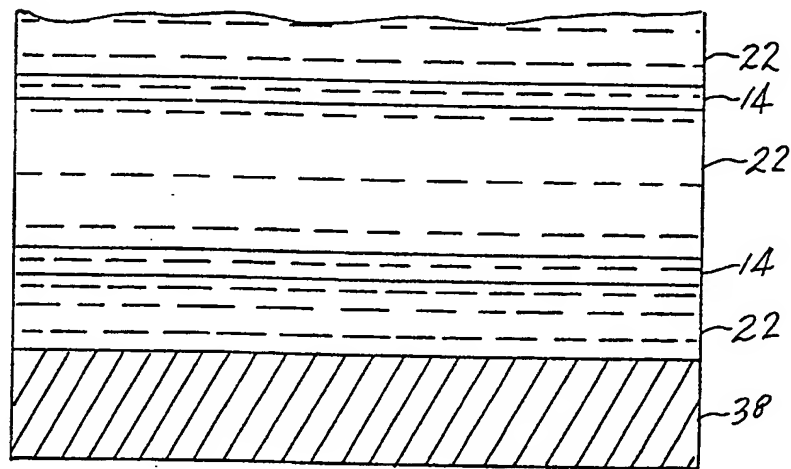


FIG. 30

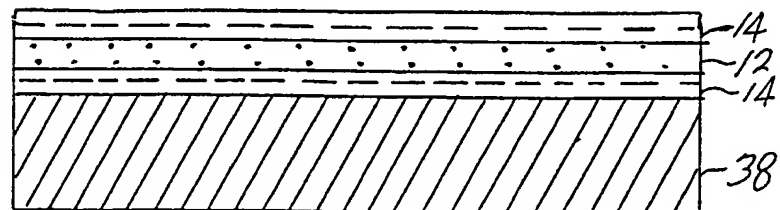
19/19



**FIG. 31**



**FIG. 32**



**FIG. 33**



# INTERNATIONAL SEARCH REPORT

International Application No.  
**PCT/US 99/25843**

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 H01L51/20 H05B33/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L G02F H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 03, 27 February 1998 (1998-02-27) -& JP 09 291356 A (ASAHI GLASS CO LTD), 11 November 1997 (1997-11-11) abstract	1, 5, 6, 8, 18, 22, 23, 28
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 641 (E-1639), 6 December 1994 (1994-12-06) -& JP 06 251631 A (KANEGAFUCHI CHEM IND CO LTD), 9 September 1994 (1994-09-09) abstract	1, 9, 10, 18, 29, 30, 35
	— -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

17 February 2000

Date of mailing of the international search report

28/02/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx 31 651 epo nl,  
Fax (+31-70) 340-3018

Authorized officer

De Laere, A

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/25843

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 582 (E-1300), 22 December 1992 (1992-12-22) -& JP 04 230906 A (UNITIKA LTD), 19 August 1992 (1992-08-19) abstract	1, 9, 10, 18, 29, 30
X	DATABASE WPI Section Ch, Week 198744 Derwent Publications Ltd., London, GB; Class A85, AN 1987-309622 XP002130779 -& JP 62 217506 A (UNITIKA LTD), 25 September 1987 (1987-09-25) abstract	1, 9, 10, 18, 29, 30, 35
A	AFFINITO J D ET AL: "A NEW METHOD FOR FABRICATING TRANSPARENT BARRIERS LAYERS" THIN SOLID FILMS, CH, ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 290/291, 15 December 1996 (1996-12-15), pages 63-67, XP000693807 ISSN: 0040-6090 the whole document	1-6, 9, 15, 16, 18-26, 29
A	US 5 547 508 A (AFFINITO JOHN D) 20 August 1996 (1996-08-20) cited in the application  column 6, line 5-7; claims	1-6, 10, 15-22, 24-26, 30, 35
A	EP 0 260 626 A (TOYO BOSEKI ; FUJIMORI KOGYO CO (JP)) 23 March 1988 (1988-03-23)  page 6, line 10-32	1, 5, 10, 18, 22, 30, 35
A	US 5 757 126 A (HARVEY III THOMAS B ET AL) 26 May 1998 (1998-05-26)  the whole document	1-6, 9-11, 18-23, 29-31, 35
A	WO 92 12219 A (MINNESOTA MINING & MFG) 23 July 1992 (1992-07-23)  page 29, line 27 -page 30, line 11	1, 6, 9-11, 18, 23, 29-31, 35
E	EP 0 977 469 A (HEWLETT PACKARD CO) 2 February 2000 (2000-02-02)  the whole document	1-4, 9, 10, 18-21, 24-26, 29, 30, 35

# INTERNATIONAL SEARCH REPORT

information on patent family members

Publication No

PCT/US 99/25843

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 09291356 A	11-11-1997	NONE	
JP 06251631 A	09-09-1994	NONE	
JP 04230906 A	19-08-1992	NONE	
JP 62217506 A	25-09-1987	NONE	
US 5547508 A	20-08-1996	US 5395644 A US 5260095 A AT 170779 T CA 2142895 A DE 69320971 D DE 69320971 T EP 0655954 A JP 8503099 T WO 9404285 A	07-03-1995 09-11-1993 15-09-1998 03-03-1994 15-10-1998 27-05-1999 07-06-1995 02-04-1996 03-03-1995
EP 0260626 A	23-03-1988	JP 2632673 B JP 63071829 A DE 3788391 D DE 3788391 T KR 9008063 B US 4802742 A	23-07-1997 01-04-1988 20-01-1994 21-04-1994 31-10-1990 07-02-1989
US 5757126 A	26-05-1998	US 5686360 A EP 0777280 A JP 9161967 A	11-11-1997 04-06-1997 20-06-1997
WO 9212219 A	23-07-1992	AU 1243092 A BR 9205462 A CA 2096826 A EP 0566683 A JP 6504387 T US 5867238 A	17-08-1992 01-03-1994 12-07-1992 27-10-1993 19-05-1994 02-02-1999
EP 0977469 A	02-02-2000	NONE	

**THIS PAGE BLANK (USPTO)**